PETROLEUM PROCESSING

VOLUME 2, NUMBER 1 JANUARY, 1947

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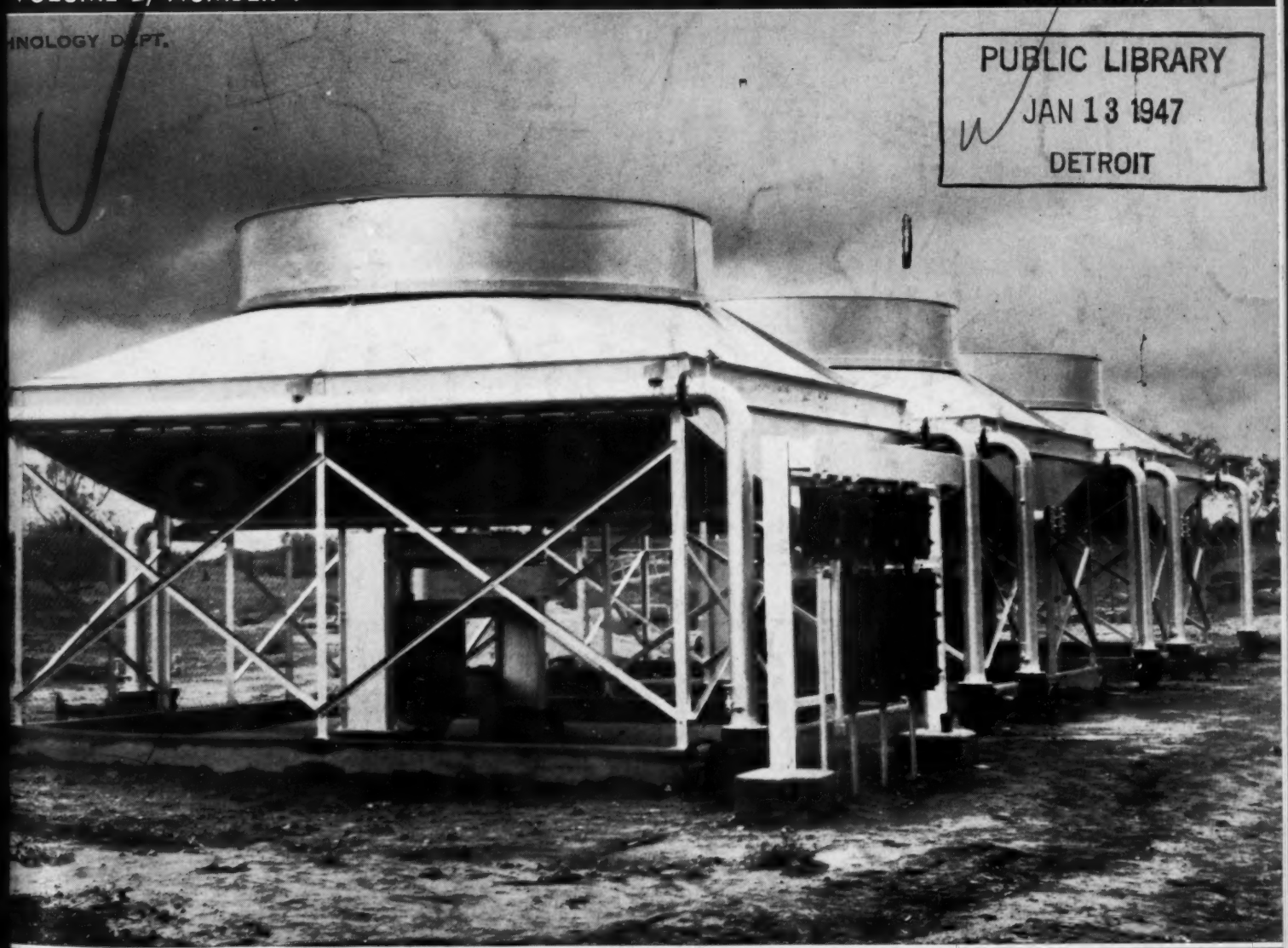

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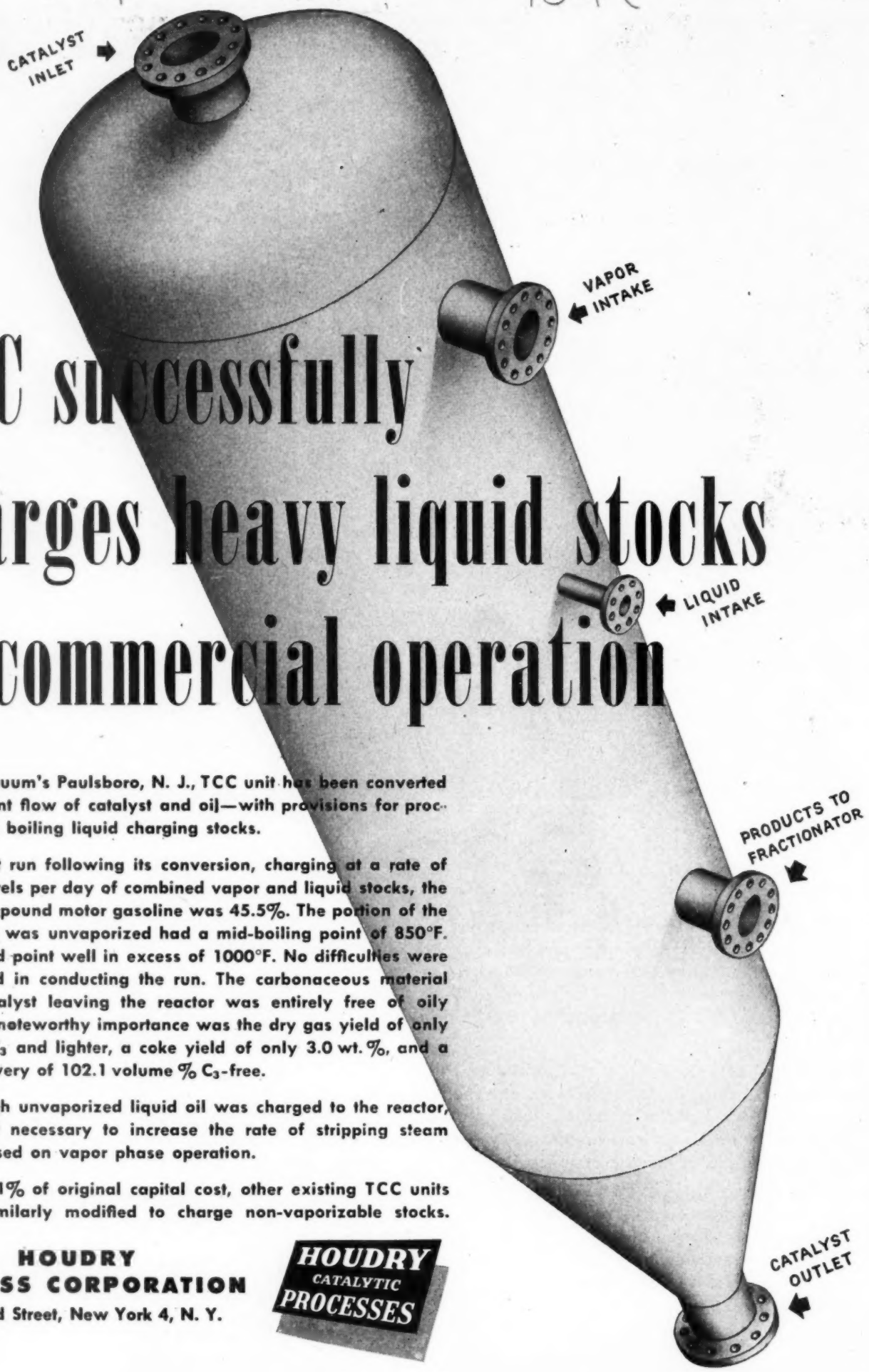

TCC successfully charges heavy liquid stocks in commercial operation

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On the first run following its conversion, charging at a rate of 10,000 barrels per day of combined vapor and liquid stocks, the yield of 10 pound motor gasoline was 45.5%. The portion of the charge that was unvaporized had a mid-boiling point of 850°F. with an end point well in excess of 1000°F. No difficulties were encountered in conducting the run. The carbonaceous material on the catalyst leaving the reactor was entirely free of oily matter. Of noteworthy importance was the dry gas yield of only 3.9 wt. % C_3 and lighter, a coke yield of only 3.0 wt. %, and a liquid recovery of 102.1 volume % C_3-free.

Even though unvaporized liquid oil was charged to the reactor, it was not necessary to increase the rate of stripping steam formerly used on vapor phase operation.

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PETROLEUM PROCESSING

Of Crude Petroleum and Natural Gas
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REFINERY OPERATION, MAINTENANCE, EQUIPMENT, DESIGN

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COMING MEETINGS

January

6-10, Society of Automotive Engineers, Annual meeting and Engineering display, Book Cadillac Hotel, Detroit.
17, Western Petroleum Refiners, Technical meeting, Washington-Youree Hotel, Shreveport, La.

February

24-28, American Society of Testing Materials, Spring meeting and Committee week, Benjamin Franklin Hotel, Philadelphia.

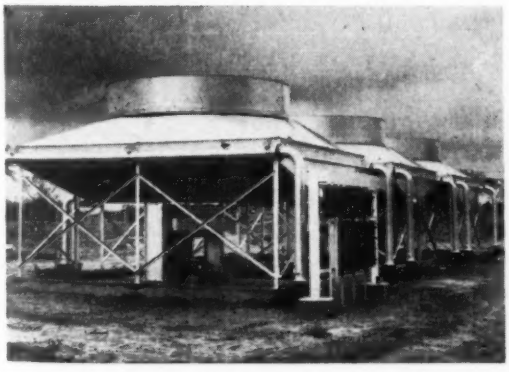
March

17-19, American Society of Lubrication Engineers, National Convention, William Penn Hotel, Pittsburgh.
17-23, American Institute of Mining and Metallurgical Engineers, Annual meeting, New York City. Technical meetings March 20-22.
22-28, American Society for Metals, Western Metals Congress and Exposition, Civic Auditorium, San Francisco.
24-26, Western Petroleum Refiners Assn., Annual membership meeting, Plaza Hotel, San Antonio.

April

7-10, National Association of Corrosion Engineers, Convention meeting, Palmer House, Chicago.
9-11, Society of Automotive Engineers, Aeronautic meeting, Hotel New Yorker, N. Y.
14-18, American Chemical Society, National meeting, Atlantic City, N. J.
23-25, Natural Gasoline Association of America, 26th Annual convention, Baker Hotel, Dallas.
30-May 2, American Gas Association, Spring meeting, Stevens Hotel, Chicago.

THIS MONTH'S COVER . . .



Photos courtesy J. F. Pritchard & Co.

Because water was scarce, the new natural gasoline plant of Warren Petroleum Corp. near Holliday, Texas, has been designed to use air as the primary cooling medium. Coolers are of the type shown above, consisting of several sections of finned tubes in the top housing cooled by a forced draft of air from motor driven fans. Details on the plant and air coolers appear in this issue of PETROLEUM PROCESSING, pg. 52

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PETROLEUM PROCESSING
JANUARY, 1947

PROPERTIES of CRACKING CATALYSTS

By Glenn M. Webb and C. H. Ehrhardt
Universal Oil Products Co.

Knowledge of the properties of solid catalysts is necessary to refiners for efficient operation of their catalytic cracking units. Detailed accurate data on catalyst life under various operating conditions, catalyst structure, surface area, mechanical strength, heat stability and so on will greatly aid in the selection of types of catalysts best suited for individual plant operations.

Much information on the subject has been developed in the research laboratories of Universal Oil Products Co. in the course of studies to improve cracking catalysts. This data is now being made available by UOP to refiners generally through PETROLEUM PROCESSING.

In this article the three basic types of available cracking catalysts are listed and their properties described in a general way. Procedures are presented by which some important characteristics are determined, as, for example, the amorphous structure of synthetic silica-alumina catalysts. Later articles to be presented will discuss detailed data on the variable properties of catalysts used in commercial cracking operations.

FOR several years cracking catalysts have been subjected to intensive investigation in the physical and chemical laboratories of the Universal Oil Products Co. Much of this work has been directed toward obtaining information that would lead to the production of new types of cracking catalysts or to improved versions of those already known. To date, virtually none of this information has been published. This series of articles is being written to present some of the properties and characteristics of these catalysts, in the belief that the availability of such information to the refiner will assist him in more intelligently meeting and solving the day-to-day problems encountered in operation of catalytic cracking units.

The purpose of this first article is to discuss the types of catalysts available and to describe their properties in a general way. Later articles will concern specific features of the synthetic catalysts that are in wide commercial use.

Types of Catalysts Available

Three basically different types of catalysts have been developed for catalytic cracking. These are (1) the natural catalysts, of which super filtrol is one of the best known; (2) silica base catalysts, typified by silica-alumina, silica-magnesia, and silica-zirconia and (3) alumina base catalysts, as exemplified by the alumina-boria catalyst.

Super Filtrol

Super filtrol is an acid-treated bentonite clay the principal constituent of which is the clay mineral, Montmorillonite. The pure mineral is ideally of the form $H_2O \cdot 4SiO_2 \cdot Al_2O_3$. The naturally occurring material frequently has some of the alumina replaced by CaO, MgO, and Fe_2O_3. The acid-leached and activated material available commercially contains all of the substances, and some other impurities as well, as shown in the following typical analysis:

Compound	%
SiO_2	66.6
Fe_2O_3	2.3
Al_2O_3	15.4
TiO_2	0.4
CaO	2.2
MgO	4.3
SO_3	3.0
Volatiles	5.8

The composition of Montmorillonite has been studied extensively, and it has been shown to have a lamellar structure with the top and bottom layers of the lamina formed of oxygen atoms. The bonding between these oxygen layers is very weak and as a result there is a large interlamellar distance.

The lamina are about 6 Angstrom* units thick and the interlamellar distance varies from about 4 to 14 Angstrom units, depending on the amount of loosely held water in the interlamellar space. This plate-like structure of Montmorillonite, which has been established from X-ray diffraction evidence, may easily be confirmed by examing it in the electron microscope. Electron micrographs of Montmorillonite show that the individual platelets may easily be distinguished. The sheets are about 50,000 Angstroms in the long direction and about 5000 Angstroms thick. An electron micrograph of a bentonite clay, taken by A. Prebus,[5] is shown in Fig. 1.

Super filtrol exhibits some interesting properties which are characteristic of the so-called "swelling" clays. Montmorillonite, being such a clay, suffers expansion and contraction of the interlamellar distance as the loosely held water content increases and decreases. For example, U. Hoffman[4] determined this interlamellar distance for a Montmorillonite containing 66% SiO_2 and 22%

TABLE 1—Effect of Water Content Upon Interlamellar Distance for Montmorillonite

Drying Temp. °C.	Water Content %	Interlamellar Distance, A
Under water	>30	19.6
Air dried	22.8	15.2
100	8.8	11.2
200	7.0	9.9
350	4.6	9.6
800	0.6	9.6

* The Angstrom unit is a measure of distance, and is customarily used in discussing properties of atoms and molecules. There are, by definition, one hundred million Angstrom units in one centimeter.

Fig. 1—Electron micrograph of Bentonite clay, showing platelike structure of its principal constituent, montmorillonite, which is also the active ingredient of natural cracking catalysts. Magnification as reproduced here is 80,000 times

Al_2O_3 (the remainder being Fe_2O_3, CaO, and MgO) with different amounts of water, with the results shown in Table 1.

Dr. Ehrhardt of the U. O. P. laboratories has checked this lattice expansion[1] for super filtrol and has obtained similar results, which are shown in Table 2.

It should be mentioned that the bentonite clays do not undergo expansion of the lattice upon absorption of water if the clay has been heated to temperatures higher than about 600° F.

The acid-leached and activated filtrols available commercially undergo profound changes in surface area, crystalline structure and catalytic activity when heated to very high temperatures. The substance is quite stable up to temperatures of about 1300° F. When the catalyst is heated at temperatures lower than 1300° F., the surface area is high (approximately 300 sq. m./g. as measured by the low temperature nitrogen adsorption method). The activity for cracking heavy petroleum oils is good and, as has already been said, its structure, as determined by X-ray diffraction methods, is the same as that of Montmorillonite.

When the mineral is heated at 1400° F. or higher, the structure simply collapses; its surface area drops to an insignificant value (−10 sq. m./g.). Its cracking activity vanishes for all practical purposes and its crystalline structure changes from that of Montmorillonite to an inactive aluminum silicate. The structure of Montmorillonite, as given by Hoffman,[3] is shown in Fig. 2.

Silica Base Catalysts

As has been mentioned above, the three main classes of synthetic silica base cracking catalysts are the silica-alumina, silica-zirconia, and silica-magnesia composites.

Two of these have been or are being produced commercially for the Universal Oil Products Co. by the American Cyanamid & Chemical Corp. and the Chicago Chemical Co. These are the silica-alumina catalysts, known as UOP Type A cracking catalysts, which were produced in very large quantities during the war for the production of aviation gasoline base stock and other components, and the silica-magnesia catalyst, designated as UOP Type Q cracking catalyst.

In addition, one other catalyst has been made in rather large pilot plant quantities by the American Cyanamid Co. It was a three-component catalyst containing silica, alumina, and zirconia, designated as UOP Type B cracking catalyst. The present discussion will be limited to the properties of the Type A (silica-alumina) and Type Q (silica-magnesia) catalysts.

Synthetic Silica-Alumina Catalysts

As would be expected, synthetic silica-alumina composites have physical and chemical properties quite different from those of the natural materials. The synthetic product has a known and definitely controlled composition. It is amorphous, has a high surface area and is very stable to heat. The type and amount of impurities present in the catalyst have a very marked influence on its catalytic properties. For example, iron is held to a very low value of 0.05% because it promotes the formation of carbon during the cracking reaction. Also, alkali metals such as sodium are not desirable since they decrease the thermal stability of the material.

Abundant evidence has been gathered to show that silica-alumina catalyst, in its active form, is amorphous. The term amorphous may be somewhat misleading for it is normally used to indicate that, by a particular test method, no evidence of crystallinity was found. In using this term in connection with silica-alumina catalysts we mean that the material is really amorphous, i.e., it has no regular structure, but, instead, resembles vitreous glass. In other words, to date, we have found indication, not that the atoms are arranged regularly, but rather that they are randomly distributed. The evidence for this view is as follows:

Many hundreds of X-ray diffraction photographs have been taken[4] of silica and silica-alumina composites. These tests have been made under conditions that reveal the presence of relatively small amounts of crystalline components, and in no case have we ever obtained a diffraction pattern showing the presence

TABLE 2—Lattice Expansion for Super Filtrol

Drying Temp. °C.	Conditions Time Hours	Volatile Content %	Interlamellar Distance, A
Under water		57.3	19.2
Partially air dried		48.2	19.2
Air dried		32.8	16.0
50	16	18.0	15.2
100	16	6.9	13.6
500	16	...	9.8
Super filtrol used in pilot plants		...	9.8

of a crystalline substance. The photographs do show the characteristic amorphous bands that silica alone, or glass, exhibits.

A somewhat more sensitive method of detecting the presence of crystalline substances than the X-ray is the electron. This is done by using electron diffraction techniques. In tests using these methods, we have again found no evidence for the presence of a crystalline phase.

The electron diffraction experiments did reveal one interesting point which is worth mentioning. This concerns the amorphous bands characteristic of silica. In 1939 Germer and Storks[2] studied thin silica films made by evaporating silica onto gold films and subsequently removing the gold base with a nitric acid-hydrochloric acid mixture. These thin silica films were then put into a high vacuum electron diffraction camera and electron diffraction photographs were taken. The films showed no sharp lines as are found with crystalline substances, but only a series of diffuse rings such as are produced by amorphous materials.

We have also made similar electron diffraction tests on our silica-alumina catalyst, and have made measurements on the diameters of the diffuse rings. These diameters can be converted to inter-atomic spacings by means of the Bragg formula. The values of these spacings, as found by Germer and Storks for evaporated silica films and by us for active silica-alumina cracking catalysts, are summarized in Table 3.

TABLE 3—Structure Measurements for Evaporated Silica Films and Active Silica-Alumina Cracking Catalysts

Band	—Spacings in Angstrom Un'ts— Germer and Storks (Silica Film)	UOP Active Silica-Alumina Catalyst
A	3.6	3-4
B	2.0	1.8-2.2
C	1.2	1.1-1.3
D	0.8	Not found

Thus, the conclusion may be drawn that the silica in the cracking catalyst has substantially the same structure as silica subjected to the very high temperatures required to vaporize it. The great difference between the two types of silica is, of course, porosity.

Glass, evaporated silica, quartz, etc., are solid, nonporous substances. The silica in the cracking catalyst is very porous, having specific surface areas as high as 600 sq. m./g. The sizes of the pores in the material are small according to ordinary standards, of the order of 50 Angstrom units. However, these openings are much larger than the gas oil molecules which must enter them to undergo reaction or the smaller molecules which are formed as a result of the catalytic reaction and must leave the catalyst.

The silica-alumina catalyst is quite stable to heat, much more so than the natural minerals. The synthetic material loses roughly only half its activity and surface area when heated in atmospheric air to temperatures as high as 1650° F. It is still amorphous after such a treatment. Indeed, the catalyst does not develop crystalline phases until the temperature has exceeded 2000° F. For all practical purposes, the material is inactive catalytically and has a very small specific surface, after it has been calcined at 1800° F. or above. Heat treatment at the higher temperatures, about 2000° F., causes complete collapse of the structure, resulting in the formation of such crystalline substances as cristobalite, a form of quartz, and mullite or sillimanite, which are aluminum silicates. The probable structure of amorphous silica is shown in Fig. 3.

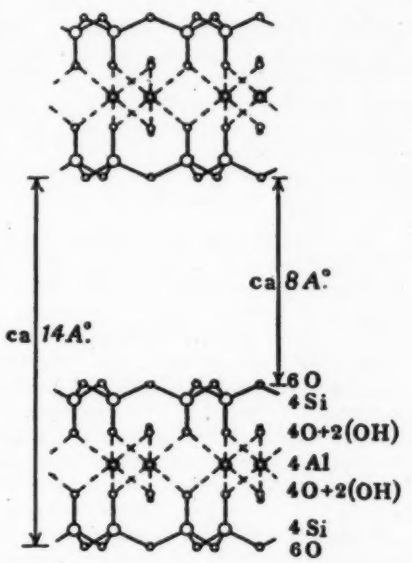

Fig. 2—Diagrammatic structure of montmorillonite, illustrating the laminar arrangement of the atoms in this material

Synthetic Silica-Magnesia Catalysts

The catalysts are similar to the silica-alumina composite in that they are synthetic products and therefore have all the advantages of easily controlled composition and reproducible physical properties. Further, both types of catalysts have in common a very active type of silica base.

The silica-magnesia catalyst has surface properties that resemble the silica-alumina catalyst. Its surface area varies from 300 to 500 sq. m./g. and the average pore diameter is in the range of 30 to 70 Angstrom units.

When the catalyst is heated to about 1400° F. it is converted into a crystalline, inactive, and relatively nonporous magnesium silicate. Thus, with respect to

Meet the Authors

Dr. Glenn M. Webb, director of the Physics Division of Universal Oil Products Co., graduated from California Institute of Technology in 1931 with B.S. degrees in physics and mathematics. Postgraduate work in the same subjects at Washington University, St. Louis, earned him the M.S. degree in 1933 and the Ph.D. degree in 1935.

Dr. Webb

From 1935-37 he was research physicist at Western Cartridge Co., East Alton, Ill., joining UOP in 1937. For a year and a half during the war Dr. Webb, in addition to his work at Universal, was engaged as a consultant on catalysts in the Manhattan atomic bomb project.

Dr. Ehrhardt

Dr. C. H. Ehrhardt, research physicist with Universal Oil Products Co., graduated in 1933 from Hillsdale College, Hillsdale, Mich., with a bachelor degree in physics. The next 5 years he spent at Purdue University as a graduate assistant in physics, earning his Ph.D. degree in 1939.

In 1940, after a few months as instructor in physics at Purdue, he joined UOP. His special fields of research work there are X-ray diffraction, electron diffraction and electron microscopy.

thermal stability, this composite behaves much more like a Montmorillonite clay than the synthetic silica-alumina product.

Alumina-Base Catalysts

Although alumina base cracking catalysts have not been used in commercial operations, it was felt that it would be desirable to mention this type of catalyst because of its interesting nonsiliceous composition.

One of the most promising alumina base catalysts contains boria deposited on the alumina. The boria content is normally in the range of 8-12% B_2O_3. Its surface area is lower than that of silica base catalysts, being of the order of 150-200 sq. m./g. and the average pore diameter is high compared to the siliceous materials, being as high as 100-120 Angstrom units.

The crystal structure of this type of catalyst is exactly the same as that of the base alumina. In other words, the only crystalline component discernible in the catalyst is gamma alumina.(4) In thermal stability it is about equivalent to the silica-magnesia and natural catalysts. It may safely be heated to about 1300° F. without in any way altering its structure; however, when temperatures of 1400° F. or higher are reached the boria reacts with the alumina to form a new, but inactive, compound containing aluminum, boron and oxygen.

The alumina-boria catalyst has one feature which makes it undesirable from the practical standpoint. This concerns the loss of boria in gases containing steam. The steam hydrates the boria to form boric acid, which is distilled off the alumina base. This means that process or regeneration gases containing steam will continually remove the boria from the catalyst, leading to a loss in activity of the catalyst and to a deposition of boric acid in the fractionators and other parts of the plants. By proper design these difficulties could probably be overcome, but up to the present writing the catalyst has not shown sufficient superiority to justify the additional expenditures that would be involved in using the catalyst.

General

In the preceding part of this paper, we have described in a general way some of the properties of the principal types of cracking catalysts. These properties, which included structure, surface area, and heat stability, are important, but they are not alone sufficient to characterize a catalyst. For example, one feature which all of these catalysts have in common is a very porous structure and a high specific surface. But it is impossible to generalize this statement and say that any cracking catalyst, to be acceptable, must have a surface area varying only between certain defined limits, or, conversely, that any material having a very high specific surface will be a good catalyst.

That this cannot be done may easily be seen from the fact that several materials are known which have high specific surfaces, but possess very little catalytic activity for cracking gas oils. Among these are silica gels (areas up to 900 sq. m./g.,), alumina gels (areas of 200-300 sq. m./g.), and charcoals (with areas up to 2000 sq. m./g.)

A similar situation exists with respect to crystalline structure. There are many materials, for example, which are amorphous in the same sense that the silica-alumina catalyst is amorphous. But this does not mean at all that they are as efficient as the silica-alumina mass for the catalytic cracking of heavy petroleum oils.

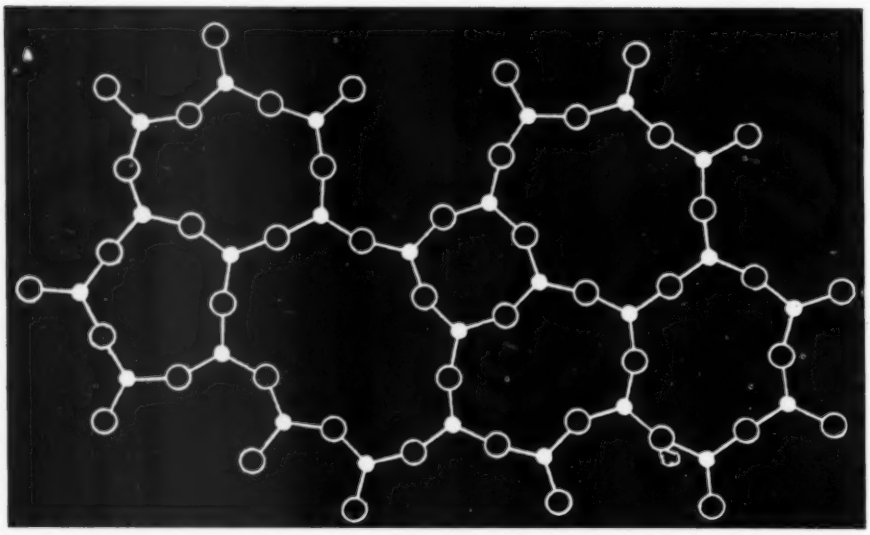

Fig. 3—Diagrammatic illustration, in two dimensions, of the probable type of arrangement of the silica (solid circle) and oxygen (open circle) atoms in silica gel

For these reasons, recourse must be had to other types of tests to characterize accurately the behavior and properties of catalysts. Foremost among these is the use of an activity test procedure that simulates at least in its important particulars the conditions to be encountered in the proposed commercial installation. In a search for new cracking catalysts this is usually the first test to be made, and normally involves passing a gas oil over the catalyst at an elevated temperature (700-1000° F.) and at substantially atmospheric pressure. The gasoline formed is removed from the entire product by distillation and its octane rating is determined.

Once a particular catalyst composition is discovered to have desirable features a great deal of involved and systematic work is required to determine its optimum characteristics. In the specific case of fixed bed catalytic cracking, for example, not only must the optimum concentration of the chemical constitutents be determined, but also the allowable type and amount of impurities, the best physical form, its strength, density, porosity, size, and so forth.

If the catalyst is to be used in the fluid type of cracking unit, some of these features must obviously be changed, notably the particle size. However, other items must be considered. Whereas the strength and density of a pelleted or extruded catalyst destined for use in a fixed bed type plant may be controlled to a certain extent by the conditions under which the material is formed, this cannot be done for fine powders to be used in a fluid unit.

In this latter case, the strength and density must be controlled at some other point in the manufacturing process, and it has been found that these properties can be altered at will in a variety of ways, such as varying the concentrations of the solutions used in making the silica gel, as well as controlling the time the gel is allowed to age before drying, the temperatures of the solutions used, and so forth.

There are also other items that must be investigated, such as minimizing the amount of carbonaceous material laid down on the catalyst, etc. It is not proposed to discuss these in the present paper, rather, it is intended only to draw attention to a few of the variables that must be explored and reserve detailed presentation and discussion of the quantitative data for the future articles of this series.

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TOMORROW

... IN PETROLEUM TECHNOLOGY

Current technological and economic developments discussed here in the light of their future bearing on petroleum refining operations include:

- **European shale-treating practice described.**
- **Shell plans production of synthetic glycerine.**
- **Gas oil polyforming offers interesting prospects.**
- **Solexol process constitutes important fat and oil refining advance**

European Shale-Treating Practice Described

As mentioned recently, the Bureau of Mines is concentrating considerable research attention on the winning of oil from oil shale. In addition to patent surveys, it has also reviewed the data on past research and commercial operations (abroad), and one of these reviews—"European Shale-Treating Practice"[1]—has recently been published as one of its Information Circular releases.

The data included "portrays at least some of the thoughts of those engaged in obtaining oil from oil shale in Europe and . . . depicts some of the results thus far obtained as well as certain plans for further efforts to win oil from shale; it is hoped that those who undertake the development of a shale-treating industry in this country will find useful information in this report.

The report describes a number of German, French, and Estonian operations and includes a literature review by the Centre D'Etudes et de Recherches des Carburants et Lubrifiants dem Remplacement on ovens and retorts for treating bituminous shales.

Of particular interest, even though its process was not in use long enough for final evaluation, is an account of a German underground shale-treating plant at Schorzingen. According to the summary of this report,[1]

"This plant heat-treated shale in underground tunnels by internal combustion methods. The oil thus recovered was appreciably less than was obtained by the laboratory Fischer-retort test. The first tunnels made were 6.5 feet wide, 7.1 feet high, and 195 feet long. The shale roofs and parts of the walls were so broken by explosive charges that there resulted a group of tunnels filled with a porous mass of broken shale approximately 195 feet long. Each of these tunnels was sealed at one end, and a coke fire was kindled at the other end to ignite the shale within the tunnel. Suction was applied at the sealed end by an exhauster, the intake of which was connected by a pipe to the sealed end of the tunnels. The evolved gases and vapors were removed through the latter pipe; the heavy oil condensed and was drained from the system."

Although this process may not prove economic, it is at least an interesting adaptation of Russian work on the underground gasification of coal and is worthy of further consideration, since the mining of oil shale presents certain difficulties not encountered in the mining of coal.

The report itself, in addition to reports on this subject released through the Office of Technical Services (PB reports), is a valuable addition to the literature on shale oil. Much has been published on this subject, but a large part of the related literature is technically and economically outdated. It is to be hoped that the Bureau of Mines' experiments, which will follow this information gathering phase, will cast more light upon a subject of much current interest and probable importance.

Shell Plans Production Of Synthetic Glycerine

After years of laboratory and pilot plant research, accompanied by detailed market studies, the Shell Chemical Corp. has recently announced that it "will begin the first commercial (domestic) production of synthetic glycerine—a goal of the chemical industry for over a century—when its projected $7,000,000 glycerine plant in Houston, Texas, is completed[2]."

That Shell was at last planning to produce synthetic glycerine on a commercial scale has been rumored rather widely during the past few months[3] [4], especially in connection with announced plans for the expansion of chemicals production at Shell's Deer Park refinery, Houston, Texas[5]. Shell has for some time been producing allyl chloride and allyl alcohol at this plant, which also produces butadiene, isopropyl alcohol, and acetone. "A $2,500,000 expansion in facilities for production of methyl ethyl ketone and secondary butyl alcohol," recently announced, is only part of a "long-range program of expansion, involving more than $25,000,000 in all, (which) will involve the erection of about a dozen individual plants, each for the production of a specific chemical[5]."

Not all the chemicals to be produced have been announced, but it has been revealed that one of them will be epichlorohydrin, another chemical which, like alklyl alcohol and allyl chloride, is part of the glycerine synthesis pattern. "The Deer Park plant will exceed in output the total of the four Pacific Coast plants of the Shell Chemical Corp. . . . Manufacture of all the chemicals will be on a large scale for bulk shipment to chemical industries making finished products. Since most of the chemicals planned for production have either been scarce in recent years or at least rather erratic in availability, the new plants are expected to have a stabilizing effect upon the field[5]."

Many of these chemicals will be produced from the propylene and ethylene available as by-products from the new catalytic cracking plant (22,000 b/d capacity) which Shell recently dedicated at its Houston refinery. Shell's plans to use this plant for the bulk production of chemicals is indicative of a trend being followed by other petroleum chemical producers, such as Carbide and Carbon, who possess plants elsewhere which produce many petroleum products, but who concentrate the manufacture of large-scale products at or near Texas refineries, where large quantities of petroleum by-products are more readily (and cheaply) available.

In further regard to the production of glycerine from petroleum, this synthesis, starting with propylene and leading through allyl chloride, allyl alcohol, etc., has been traced elsewhere too many times to be newsworthy here[6]. Shell has long ago developed this process through the pilot plant stage, and has evidently decided that future market conditions warrant its commercial use. No official announcement of the plant's capacity has yet appeared, but rumors for a $5,000,000 plant (evidently somewhat incorrect) mentioned a rated annual capacity of 30,000,000-35,000,000 lb. per year of refined glycerine[3], [4].

"But whether the synthetic plant would make 25,000,000 lb. or 35,000,000 lb. from propylene a year, it is interesting to

(1) Odell, W. M. and Baldeschwieler, E. L. *European Shale-Treating Practice*, U. S. Bureau of Mines Information Circular 7348, Washington, 1946.

(2) Anon., National Petroleum News 38, No. 49, 46 (1946), "New Shell Plant at Houston to Make Synthetic Glycerine."

(3) Anon., *Chemical Industries* 59, No. 3, 539 (1946), "Glycerine Enters New Era."

(4) Stenerson, H., *Chemical and Engineering News* 24, No. 18, 2565 (1946), "Behind the Markets."

(5) Anon., *Chemical and Engineering News* 24, No. 21, 2926 (1946), "Industrial News."

(6) Williams, E. C. et al, *Chemical & Metallurgical Engineering* 47, 834 (1940); 48, 87 (1941), "Synthetic Glycerine from Petroleum."

compare this reported planned output with the production of by-product glycerine. In 1941, before the oils and fats shortage became severe as the result of the suspension of coconut oil and other vegetable oil imports, production of C. P. glycerine on a 100% basis amounted to 108,112,000 lb. By 1943, it had slumped to 63,242,000 lb., and through such heroic measures as household fats salvage, C. P. production recovered during 1944 to 99,205,000 lb. Last year the output fell off again to 83,284,000 lb. . . . Crude glycerine production has followed about the same trend. The output in 1941 amounted to 195,283,000 lb., 100% basis, and last year was 172,450,000 lb.[4]."

Although glycerine is used in innumerable industries, "a full one-half of domestic consumption is channeled to alkyd resins, coating materials such as cellophane and parchment, tobacco, and explosives. The first two industries are new and expanding. . . .

"Quotations on the C. P. grade over the years 1920-1940 have averaged about 16 cents per lb. During this period there have been three peaks, at 28 cents in 1930; 32 cents during 1926-27; and 29 cents during 1937. The lowest trough was reached, following a gradual decline in the post-1929 depression years, at a price of 10 cents in 1933. Today, glycerine sells at 18½ cents, but producers are pressing for an increased ceiling (this was written before the end of price control)[3]."

Natural glycerine is an unavoidable by-product of soap and fatty acid manufacture; its economics, therefore, are closely related to these materials (particularly soap). Output from these sources appears to have leveled off at a peak of 200,000,000 lb. per year, and it is to fill an anticipated shortage that Shell's glycerine plant appear particularly economic, since there is certainly no assurance that synthetic prices will be able to undercut market levels. Synthesis from petroleum appears to have in its power to stabilize prices and "to guarantee a virtually inexhaustible potential supply of high-grade glycerine at a basic price. This realization should act as a stimulus to industrial developments leading to new and wider uses for glycerine; developments which might not be embarked upon in the absence of such guarantees[3]."

Gas Oil Polyforming Offers Interesting Prospects

THE lifting of war-imposed censorship has certainly permitted technical meetings of petroleum organizations to hear papers of better quality as regards technical details, as was evidenced by the recent API meeting in Chicago. Of particular interest at this meeting were the papers on the Polyform Process which, while known and used before the war, underwent considerable development during the war period[7].

Naphtha polyforming undoubtedly fills a need which many refiners have felt, and its potentialities for gasoline production from excess refinery gases (which may be charged along with the naphtha and recycle gases) are undoubtedly of considerable importance. Of particular interest, however, is an item reported last month by one of PETROLEUM PROCESSING's editors:

"In addition to the work which has been reported on naphtha polyforming, Gulf engineers told PETROLEUM PROCESSING that they are also conducing studies on gas oil polyforming which are reported to show promise of giving the refining industry another tool for increasing yields and octane number. By this process, according to the engineers, a light paraffinic gas oil (up to 700° E. P.) can be converted to gasoline with a yield of 60-70% and an octane of 73-76, motor method, or a light catalytic recycle stock or light naphthenic gas oil can be processed to 50-60% yields of 78-82 octane. These yields with gas oil polyforming are all based on once-through operations. Refinery or outside gases can be charged with these stocks equally as well as with naphtha."

No process conditions are mentioned, but it may be noted that those for naphtha polyforming approximate 1025-1125° F. outlet temperatures and 1,000-2,000 psi. pressures. While thermal cracking, alkylation, and polymerization are probably the basic reactions involved, it is interesting to note that the process bears some resemblance to attempts at destructive hydrogenation with hydrocarbon gases instead of hydrogen.

Process conditions differ somewhat, of course, but it may very well be that experiments of this type will serve to shed light on what could be a very important advance in refining art. One of the two chief economic deterrents to the use of destructive hydrogenation has been the high cost of equipment; the other has been the (comparatively) high cost of hydrogen. The lower hydro-carbons—methane, particularly, but also ethane, propane, and butane—cost less than hydrogen, are abundantly available, and, most important, are rich in hydrogen. For this reason, some desultory research has already been conducted on their use as destructive hydrogenating agents, with inconclusive but by no means discouraging results.

Meanwhile, gas oil polyforming would be an important step in petroleum refining and would warrant attention on its own merits. More information on this subject will be awaited with impatience.

(7) Offutt, W. C., Ostergaard, P., Fogle, M. C., and Beuther, H., PETROLEUM PROCESSING 1, No. 4, 267 (1946), "Naphtha Polyforming"; Offutt, W. C. et al, *Ibid.* 1, No. 4, 278 (1946), "Naphtha Polyforming with Outside Gas"; and Hirsch, J. H. et al, *this issue*, p. 61, "Correlation of Operating Variables in the Polyform Process."

(8) Bland, W. F., PETROLEUM PROCESSING 1, No. 4, 243 (1946), "Polyform Process Utilizes Excess Gases in Upgrading Naphthas and Gasolines."

Solexol Process Advances Fat and Oil Refining Art

PROPANE deasphalting has long been an important lubricant refining method and has, in the past few years, been used in the preparation of heavy catalytic cracking feedstocks. Allied processes include propane dewaxing and propane-deresining—in fact, a whole art of petroleum separation (according to hydrocarbon structure) is possible with the use of propane (or similar light hydrocarbons) at appropriate temperatures and pressures. In such processes, liquid propane serves as an anti-solvent, precipitating out the desired substances under specific conditions; i.e., an asphaltic residuum which is entirely soluble in liquid propane at low temperatures precipitates its asphalt as the temperature is raised (under such pressures as are needed to keep the propane in the liquid phase).

The M. W. Kellogg Co. has been the chief builder of propane deasphalting plants, so that there is perhaps no great surprise to learn that this company is now constructing seven plants which apply propane refining to the purification (separation) of oils and fats, by the "Solexol process[9]."

As in the case of petroleum, liquid petroleum at low temperatures mixes in all proportions with glyceride oils and fats. "As the temperature is raised, however, the capacity of the propane to mix with oil components of high molecular weight decreases, and these components are progressively precipitated." By the time the critical temperature of propane is reached, almost every component has been precipitated; "thus a selective extraction of desired quantities of material can be effected by raising the temperature and bringing the oil-propane mixture into equilibrium."

"Temperatures required are well below those used in most (oil and fat) refining techniques," thus preventing polymerization of oil constituents and preserving vitamin content. Processing costs for this continuous process are said to range from "as low as a fraction of a cent to three cents per gallon of oil processed."

Kellogg believes that this process "will foster development of several new oil products for industry, improve the quality of current oil products, and make possible economies running into millions of dollars yearly in the refining of some 25 basic vegetable, animal, and marine oils and fats." For example, crude soybean oil "can be separated so that 67.5% of the original quantity is an edible oil suitable for shortening, margarine, and salad oils. Another 30% is suitable for paints, varnishes, enamel, oilcloth, printing inks, and alkyd resins; 1.5% contains color pigments in highly concentrated form, plus lecithin; and the remaining 1% is rich in sterols useful for synthesis of hormones and other pharmaceuticals."

(9) Anon., *Business Week*, No. 899, 48 (1946), "Industrial Oils Advance."

Delayed Coking Unit Processes Residuum Into Gas Oil Charge for TCC Unit

By RANDAL MAASS and R. E. LAUTERBACH General Petroleum Corp.

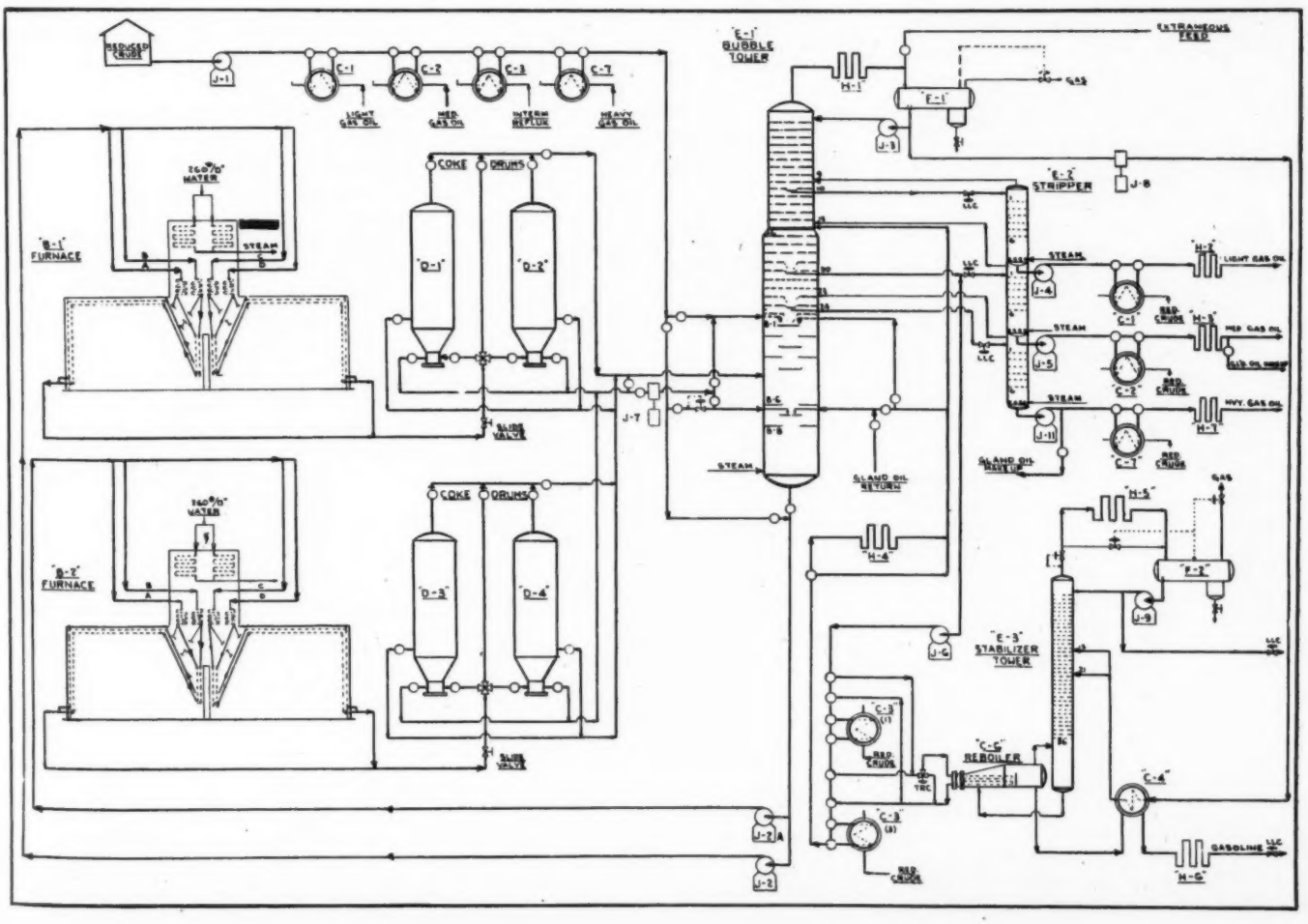
WITH the Diesel engine, household burner, and light oil cracking units all competing for the intermediate or gas oil fractions, the general trend in refining is toward a more extensive cracking of the residuum fraction. It has been estimated that this trend in the next 10 or 20 years will reduce the percentage residuum from the present 26% to some 10%. It is not expected that this cracking of heavier stock will so much replace light oil cracking as that it will provide the requisite charge stock.

The General Petroleum Corp. has contributed to this trend by installing a 15,000 b/d delayed coking unit to process 300-700 sec. (SF/122°F.) viscosity straight-run residuum. The gas oil thereby obtained will serve as part of the feed stock to General's four Thermofor Catalytic Cracking units. The coking unit was designed, engineered and constructed by the M. W. Kellogg Co., and is the largest of its kind in the world. Operations started July 26, 1946.

General Process

The description of the general process may best be followed by referring to the flow sheet, Fig. 1. The cracking portion of the coking unit is divided into two sections, each with its own furnace and pair of coke drums to be used alternately. The cracked products from the two cracking sections enter a common bubble tower for fractionation into an overhead product of gasoline and lighter, three gas oil draw products, and a bottoms recycle product. The straight-run residuum charge, or reduced crude charge, as it is called, is introduced into the bubble tower for further fractionation, with the bulk of it appearing in the bottoms for furnace charge. Three steam strippers for the side draw streams and a gasoline debutanizer complete the fractionation equipment.

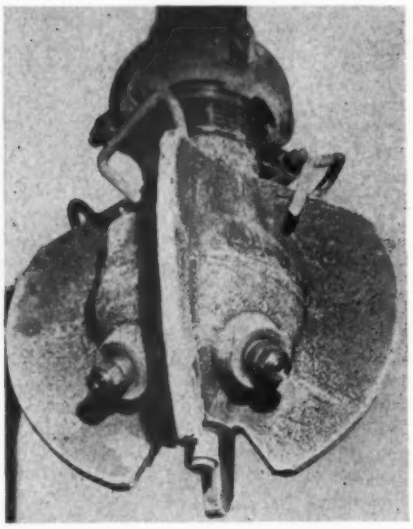
Fig. 1—General schematic flow diagram of the new delayed coking unit at General Petroleum's plant



Physical Equipment

Furnaces

As was indicated above, two duplicate furnaces have been provided, one for each pair of coke drums. The distinguishing and highly desirable feature of a delayed coking unit is the delaying of the coking until the charge reaches the soaking chamber (coke drum). To accomplish this the furnaces are designed for a low residence time and consequently a high rate of heat pickup. Because of the high heat level (600° F.) of the furnace charge, the oil tubes were restricted to the radiant section and the hotter



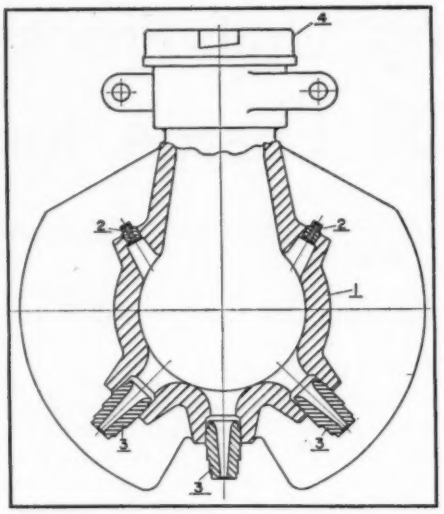


Fig. 2—Head of boring tool assembly for removing coke from the coke drums at General Petroleum's new delayed coking unit. In the drawing, 1 is the first boring tool, complete; 2 the cleaning nozzles; 3 the boring nozzles; and 4 the lower half of the coupling

portion of the convection section. Heat economy is realized through the use of water tubes for steam production in the colder portion of the convection bank.

In general each furnace has four separate coils which join outside the firebox into a common transfer line. The 3¼-in. O. D. tubes are 42 ft. long and have a wall thickness of 7/16 in. Alloy tubes of 9 Cr-1.5 Mo are used in the radiant section and to shield the convection bank. The remaining tubes in the convection bank are 5 Cr-0.5 Mo. Heat is supplied by 16 Zink combination oil and gas burners located in the end of the firebox.

Waste Heat Boiler

As was indicated above, the temperature of the furnace charge was too high to realize a good heat economy with oil tubes alone. Therefore, a waste heat boiler, with its lower receiving temperature, has been added in the convection bank of each furnace to reduce the temperature of the flue gases. This heat pickup serves to supply some 75% of the plant's steam requirement. The outlet of the coils from the two furnaces enters a common steam drum from which a single boiler feed pump takes suction to circulate the water through both coils. A level control maintains the water level in the drum by admitting treated water from the refinery main boiler plant feed pumps.

Coke Drums

Continuity of operation is maintained through the use of a pair of coke drums for each furnace, one drum being in coking service while the other is being decoked. Each drum is 17 ft. in diameter and 80 ft. in height with 61 ft. of straight section. For protection against corrosion the vessels are lined with a 7/64-in. thickness of Type 405 stainless steel, the lining being resistance welded to the shell. In addition the upper half of the shell is ⅞-in. thick and the bottom half 1 in. thick.

Alloy steels were also used in the principal piping to and from the coke drums. The transfer lines were fabricated from 9 Cr-1Mo pipe and the vapor lines from the drums to the bubble tower from 5 Cr-0.5 Mo. Portions of the drum condensate lines, the side vapor lines and the by-pass lines are also of alloy steel.

Bubble Tower

The 100-ft. bubble tower is 11 ft. in diameter in its upper section and in its bottom section is enlarged to 12 ft., 6 in. to accommodate the increased downflow occasioned by the introduction of the intermediate reflux and the reduced crude feed. Fifteen cast iron bubble trays are used in the upper section and in the lower section ten Type 405 stainless steel bubble trays with eight cast iron baffle trays below them in the potential coking region. The shell thickness varies from 9/16 in. to 5/16 in. and is protected throughout by a 7/16-in. Type 405 stainless steel strip-welded lining.

To reduce construction costs the three sidedraw steam strippers are contained in one 4-ft. 6-in. by 56-ft. shell appropriately divided into three sections, each with six bubble trays. The available hydrostatic heads dictate that the strippers be used in the same vertical order as the draw; that is, with the top draw in the top stripper, etc. The strippers are unlined and the trays are all cast iron.

The entire hot oil section of the plant is protected from corrosion through the use of alloy steels. In the bubble tower region, however, some exceptions were made after considering the corrosion tendency and ease of replacement.

Debutanizer

The design of the 4-ft., 36-bubble tray debutanizer follows the conventional pattern. The tower is unlined and all trays are cast iron. To accommodate possible depropanization, the design working pressure was set at 330 psi.

Heat Exchange Equipment

Characteristics of the shell and tube heat exchangers are given in Table 1. Following our general practice open section condensing and cooling equipment is used throughout. Open sections, located in a 45-bay atmospheric cooling tower, were provided as shown in Table 2.

Decoking Equipment

Coke is removed from the drums by a water jet designed by the Worthington Pump & Machinery Corp., which cuts the body of coke into pieces small enough to fall into a crusher car. The crusher car breaks the pieces of coke

TABLE 1—Shell and Tube Heat Exchangers

Shell Side	Tube Side	No. of Bundles	Total Surface sq. ft.	Tube Material
Reduced crude	Light gas oil	2	2,480	Steel
Reduced crude	Heavy gas oil	2	2,480	Steel
Reduced crude	Intermed. reflux	4	12,880	Steel
Reduced crude	Fuel oil	2	4,350	Steel
Stabilized gasoline	Stabilizer feed	2	1,090	Steel
Stabilizer bottoms (Stabilizer reboiler)	Intermed. reflux	1	2,000	Steel

TABLE 2—Condensing and Cooling Equipment

Service	No. of Bundles	Total Surface sq. ft.	Tube Material
Bubble tower overhead	18	10,200	Admiralty brass
Light gas oil	4	2,020	Admiralty brass
Heavy gas oil	6	3,030	Red brass clad steel
Intermediate reflux	2	1,140	Admiralty brass
Stabilizer overhead	4	2,280	Admiralty brass
Stabilizer bottoms	1	530	Admiralty brass
Fuel oil	8	4,660	Red brass clad steel
Gland oil	2	1,060	Admiralty brass
Gland water	2	1,140	Admiralty brass

down to a maximum dimension of 5 in. and feeds the sized coke into a sluice.

The coke is sluiced with water into a suction pit from which a coke-water slurry is pumped through a 12-in. line to the storage area. Here the bulk of the coke is separated from the water and then moved to a convenient location for shipping.

The decoking water jet is supplied by a centrifugal five-stage volute pump with external interstage passages. An hydraulically balanced rotor was obtained by providing double inlets at the first stage and by placing the remaining four single-inlet stages back to back. The double inlet at the first stage also provides a low inlet velocity which permits operation at a low submergence. All impellers are of the enclosed type. A pressure breakdown bushing is provided at the inboard stuffing box so that both stuffing boxes are under suction pressure. The 4000 rpm 1450 hp. turbine drive is supplied with 165-lb. 100° F. superheated steam and exhausts to a 26-in. Hg vacuum provided by a barometric condenser.

Two complete pumping units are provided; one will supply 1100 gpm. at 1500 lbs: two in parallel will supply 1600 gpm. at the same pressure. Electrically powered block valves, located in the discharge line, operate so as to prevent a shut-off against the pump. When the main block valve begins to close a smaller bypass valve begins to open so as to discharge the water back to the suction tank. In reverse the valve operation affords the same protection. From the pump discharge the jet water flows to a manifold at the top of the coke drum.

A 100-ft. derrick structure is mounted over each pair of coke drums to support the drilling equipment. Each drilling assembly includes a continuous length of drill stem long enough to reach the whole length of the drum and to which the boring and cutting tools can be attached. The drill stem is coupled at the top to a swivel head which is rotated by an air motor and which can be raised or lowered by a steam winch. An assembly of Chicksan joints forms a flexible connection to supply jet water to the swivel head. Lock valves have been provided in the jet water lines to each drilling assembly. These valves are closed whenever the drill stem is removed from the drum so that no one would be injured if the high-pressure water were inadvertently turned on.

The cutting devices for removing coke are a boring tool, reaming tool, and cutting tool. The boring head which is illustrated in Fig. 2 is essentially a round ball about 10 in. in diameter which is tapped for water nozzles. One ½-in. nozzle is located in the bottom to direct a jet straight downward, and four ⅜-in. jets are symmetrically arranged about it to direct the water downward at about 45° from the vertical. Two ⅛-in. jets are directed upward to keep any coke fines from settling on top of the tool and stopping its rotation.

For reaming, the same tool is used, except that the bottom jet is removed and plugged off, and the four ⅜-in. nozzles are replaced with ½-in. nozzles.

The cutting tool shown in Fig. 3 is an hydraulically designed assembly which splits the single stream of water in the drill stem into four jet streams. Two streams are projected horizontally at the top of the tool and the other two at the bottom are directed upward at such an angle that they cut the same plane as the horizontal jets at the surface of the coke drum, or at a distance of 8½ ft. from the axis of the drum. The nozzle tips in this tool are replaceable and at the present time ⅝-in. tips are used in the bottom nozzles, while 7/16-in. tips are used in the top.

The crusher car, which grinds the coke to a size easily pumpable by the coke pump, consists of an 11 x 14-ft. hopper which feeds the coke to two 2-ft. dia. by 5-ft. long toothed rolls spaced 5 in. apart. The rolls are driven by a 40-hp. motor. The crusher car is mounted on wheels and a track so it can be positioned beneath any of the four drums. A "grizzly" fabricated of 1 x 8-in. plate, has been added near the top of the hopper to keep any large chunks from bridging over the crusher rolls or damaging them by impact.

The crushed coke and the water from the jets pass between the rolls into a sluice which lead to a coke sump. Additional sluice water is added to the ditch as needed to keep the coke and water from piling up under the crusher car. An Allen-Sherman-Hoff Hydroseal coke slurry pump, located in a pit adjoining the coke sump, pumps the coke-water slurry through a 12-in. line to the coke storage area located some 2500 ft. from the pump. The pump derives its name from the clean water supplied to the case to seal the impeller. This water also serves to flush grit away from the close clearance area between the impeller shrouds, shaft, and suction eye and the rubber lining provided in that area. The speed of rotation of the pump can be varied by means of an adjustable sheave on the motor and three sizes of sheaves on the pump. At 600 rpm. the pump will discharge about 3000 gpm. of water over a coke outlet some 38 ft. above its suction nozzle through the 12-in. line.

Special hydraulic lift cars were designed to raise and lower the heavy bottom heads of the coke drums. Had only one car been provided, the track system would have been needlessly complicated to permit moving one car past the other. This complication was avoided by providing cars to be placed on the single track on both sides of the crusher car. Also, with two cars, two drum heads can be worked on at the same time. The hydraulic lifts operate on 90-lb. water and are individually capable of supporting the bottom head plus the drum height of water.

Operation of the Unit

Feed Introduction

Reduced crude is charged to the bubble tower by Quimby screw-type charge pumps under control of a flow-controller which regulate the rate by positioning a by-pass valve between the pump discharge and suction. The reduced crude is preheated by exchange successively with the light gas oil product, the medium gas oil product, the intermediate reflux stream, and the heavy

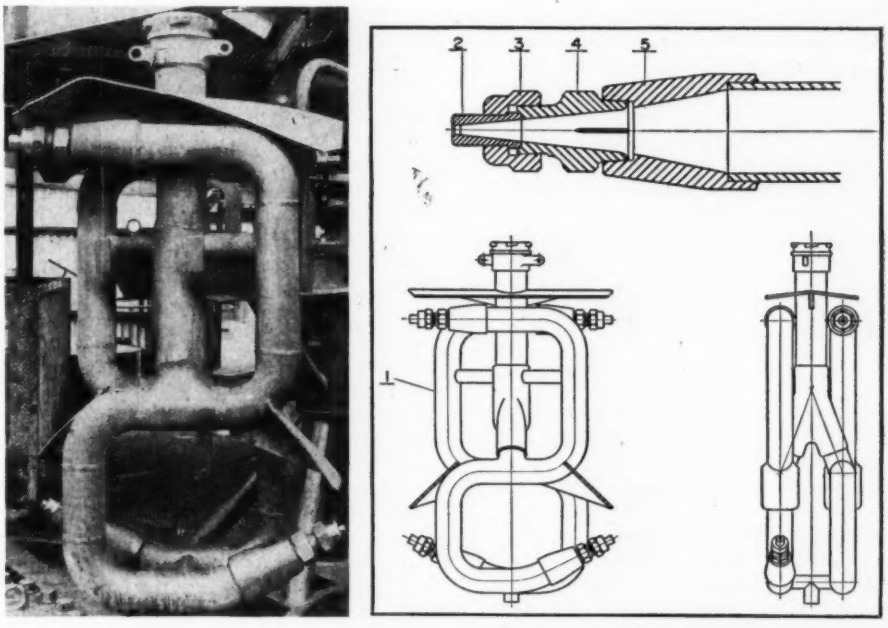
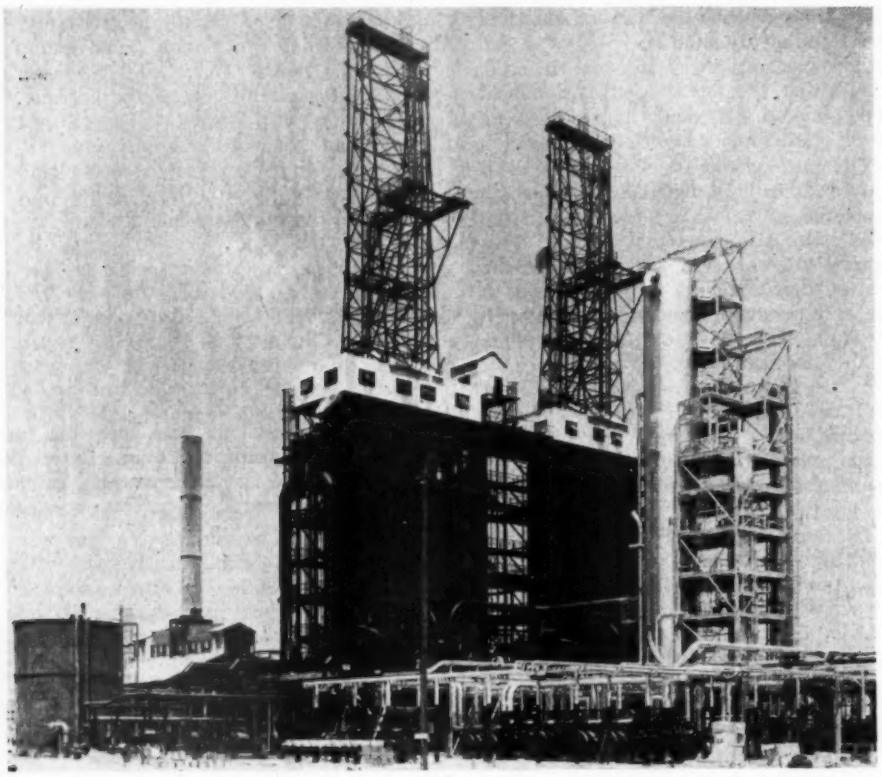


Fig. 3—Assembly of final cutting tool for removing coke from the coke drums. In the drawing, 1 is the tool complete; 2 the nozzle tip; 3 the nozzle cap; 4 the nozzle body; and 5 the nozzle body adapter



General View of General Petroleum's 15,000 b/d delayed coking unit, showing the 100-ft. derricks atop each pair of coke drums for supporting the drilling equipment used to remove the coke. At the right is the fractionating equipment

gas oil product. It enters the bubble tower at two points, at the top baffle tray or five baffle trays above the cracked vapor inlet and at the second baffle tray from the bottom or two baffle trays below the cracked vapor inlet.

With a preheat level of only 450° F. the feed serves as a hot reflux and care must be exercised to avoid transferring so much heat to the tower bottom product, through a contact with the cracked vapors (the sole source of fractionating heat), as to impair fractionation in the tower. This condition is avoided by temperature controlling the flow of reduced crude to the top inlet so as to maintain a constant temperature on the bottom bubble tray. The excess feed is diverted by a pressure controller to the lower inlet. Any feed thus diverted also serves to subcool the tower bottom and thereby reduces the tendency to form coke in this reservoir.

Heating

Both furnace charge pumps take suction off the tower bottom to deliver the charge to the four parallel coils in each furnace. The radiant section of each furnace is divided into two combustion chambers containing two of the coils. The charge flow is rate controlled to each half of the furnace and the fires in each combustion chamber are separately controlled to maintain a constant temperature at the combined outlet of each pair of coils. The two temperature controlled outlets from each furnace join in a furnace transfer line which discharges into one of the two coke drums allocated to each furnace.

Coking

The heated mixture of vapor and liquid from the furnace enters the bottom of the coke drum. Since only vapors can pass out the top of the drum, any liquid must remain in the drum until it is cracked to vapors and coke. As coke is deposited the incoming liquid and vapor must flow through the coke bed and through or into the liquid on top of the coke. With vapors and liquid continually flowing through the coking region, the coke deposited is of a highly porous nature, which facilitates subsequent handling and contributes to the quality of the product. Each drum remains on the line for 24 hrs., during which time approximately 250 tons are therein deposited.

Fractionation

The vapors from the two drums currently in simultaneous operation enter the buble tower between the fifth and sixth baffle trays, numbering from the top. As previously mentioned, this stream supplies the sole source of fractionating heat to the tower. The top temperature of the tower is controlled, by means of vaporizing reflux, to pass the gasoline and lighter streams overhead. A portion of the downflow induced by the top reflux is removed from the tenth bubble tray, steam stripped, and delivered to storage, after heat exchange and cooling, as light gas oil. The remaining down flow is augmented at the 15th bubble tray by an intermediate reflux stream and by the additional reflux thereby induced.

To handle this additional flow the tower is enlarged at the 15th tray from 11 to 12 ft. 6-in. in diameter. The intermediate reflux is removed from the 20th bubble tray to be cooled by heat exchange with the fresh feed, by supplying heat to the debutanizer reboiler, and by exchange with cooling water if necessary. The intermediate reflux returned to the 15th tray is rate controlled. Should it be desirable to reduce the down flow on the lower bubble trays some intermediate reflux can be manually controlled to the first baffle tray.

As an added means of reducing the coking tendency in the bottom two baffle trays and the tower bottom reservoir, provision has been made to manually control some of this reflux to the seventh baffle tray if needed. The intermediate reflux draw is also used to remove the medium gas oil product which is stripped and cooled. The heavy gas oil, which is also stripped and cooled, is withdrawn from the 24th bubble tray.

The preheated fresh feed is added to the first baffle tray as required to maintain a constant temperature on the 25th or bottom bubble tray, the remaining feed being diverted to the seventh baffle tray. The tower bottoms, which include the fresh feed and recycle, are rate controlled to the furnaces. The lowest sidedraw is withdrawn at the rate required to maintain the tower bottom level. Under this arrangement, with a constant 20,000 b/d charge to the furnaces, the recycle rate is automatically determined as the difference between the fresh feed rate and the total furnace charge.

The bubble tower overhead is cooled and condensed in the cooling tower and is separated into gas and gasoline in the reflux accumulator. The gas flows through a back pressure controller to the refinery central compressor station, where it is compressed to the central absorption plant pressure. This controller sets the pressure for the entire system so that the pressure on the coke drums and the bubble tower is but 2-4 lbs. higher than the 52 lbs. held on the bubble tower reflux accumulator. The resulting pressure at the furnace outlet rides at about 75 lbs.

The stripping and coke drum cooling steam are also condensed in the overhead condensers and removed from the accumulator through a bottom boot. The hydrogen sulphide content is so high that this water must be steam stripped in the refinery central deodorizer before it can be delivered to sewer.

Gasoline reflux is pumped back to the top of the bubble tower under control of a temperature element located in the vapor space above bubble tray No. 2. The net gasoline make is charged to the debutanizer after heat exchange with the debutanized gasoline. The raw B-B is delivered to raw B-B storage for ultimate alkylation plant feed and the uncondensed

vapors to the central gas plant under its own pressure. For more precise control the tower pressure is maintained by a vapor line regulator. In order to insure a steady reflux pressure and thereby smooth out reflux flow, the accumulator pressure also is controlled within narrow limits through the use of a repressuring controller, which bypasses vapors around the condensers to maintain the accumulator pressure, and a depressuring controller, which relieves the excess pressure to the gas plant.

Reboil heat is obtained from the intermediate reflux stream. To reduce the tendency to polymerize the cracked gasoline, it was decided to hold the temperature of the heating stream to 600° F. or below. Since this stream runs close to 700° F., it is first passed through the first of its four heat exchangers and is satisfactorily cooled by exchange with the fresh feed. A temperature element on the 34th tray controls the quantity of heating oil to the reboiler by positioning a three-way control valve. After passing through the reboiler, or by-passing it, the intermediate reflux stream is further heat exchanged against the fresh feed in the remaining three exchangers and cooled if necessary before it is returned to the bubble tower.

Coking Drum Cycle

Operation of the coke drums requires that the furnace transfer line product be switched from one drum to another whenever a drum is filled with coke to the desired outage. At normal feed rates each drum is on stream coking for 24 hrs. and is off stream for cooling, decoking and heating up for the same period. The drum switches are so timed that one of each pair of drums comes off stream every 12 hrs. Under normal conditions the cycle for one drum is about as given in Table 3.

The transfer line from each furnace is connected to a three-way switch valve which diverts the transfer line product to either coke drum or through a by-pass line to the bubble tower. Before switching the oil from one drum to another, the empty drum is preheated by forcing some vapors from the on-stream drum into the top and pumping the condensate from the bottom of the drum into the bubble tower.

Whenever the oil stream is switched from a full to an empty drum, the full drum must be purged of volatile oils and cooled down so that decoking operations can be started. After switching out of a drum, steam is immediately cut into it, both into the transfer line to the bottom of the drum and into a steam ring just above the bottom cone. The full drum is steamed to the bubble tower for 30 min. and is then depressured to the blowdown system. After 15 min. steaming to the blowdown, the steam is cut out and water pumped to the steam ring.

This cooling produces considerable steam which must be handled in the blowdown system located about 2000 ft. from the unit area. The blowdown line exhausts into a small tank about 6 ft. below a water level maintained by a continuous circulation through the tank. The circulation is sufficient to remove the superheat of the steam and to condense any oil vapors. Some saturated steam is vented from an 80-ft. stack mounted on the tank. The overflow from the tank runs into a skimming sump to remove any oil. The sump water is cooled by circulation over a 2-bay cooling tower, and a portion of the circulating water is diverted through the blowdown tank to maintain the level. The cooling tower was not designed to handle the instantaneous heat load, but rather the average heat load, the volume of water in the system acting as a flywheel or heat reservoir.

When the coke bed has been cooled to 200-300° F. the cooling water is cut out and the drum drained. It is then ready for the decoking crew to start blinding off, opening the heads, and removing the coke.

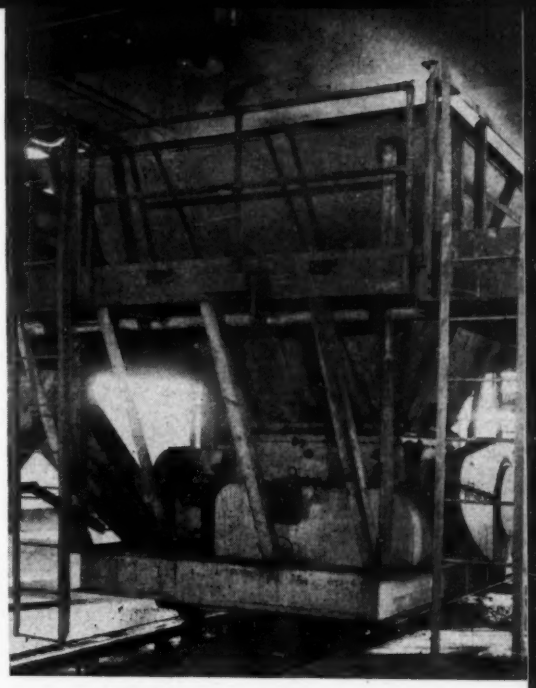
Operation of Decoking Equipment

After a drum is cooled and drained the lines leading to the drum are blinded and the manheads removed. With the crusher car positioned under the drum, the boring is begun with the stem rotating at about 8-10 rpm. The drill is lowered as fast as possible without allowing the boring tool to actually touch the coke bed. Normally about 15 min. are required for the high velocity water to cut a hole through the coke. Some water leaks through the bed while drilling, but the majority is held up in the drum until the tool breaks through at the bottom. In the meantime the coke pump is started up and water alone is discharged through the coke line to the storage area until the boring operation is completed.

After the boring is completed, the reaming tool is moved slowly up and down until the hole has been enlarged to about 6 ft. in diameter. This operation requires from 45 min. to 2 hrs.

After reaming, the cutting tool is installed and the final cutting is begun with the drill stem rotating at about 5-10 rpm. The coke is cut from the top of the bed and falls down through the hole into the crusher car. It is usual to lower the tool about 8 in. at a time and rotate it for 2-3 min. before again lowering. Every 5-10 ft. the jet is shut off and the drum inspected for cleanliness. It has been found necessary to remove the coke completely on the way down since any ledges left behind for later removal will frequently fall into the crusher car and plug up the top grating or will bridge across the bottom of the drum.

Occasionally the coke is cut from the drum at such a rate that the coke pump, operating at medium speed, will not handle it. When this occurs the cutting rate is lowered by reducing the depth of cut until the excess coke is pumped away. The pump can be set to pump at a faster rate, but it is felt that a good average speed has been fixed which does not unduly delay the coking and which does not pump too much water when the cutting rate is lowered as hard coke is encountered. It is also possible to cut coke so fast that the resulting large chucks cannot be handled by the crusher.



Coke is removed from the coke drums by water jets, which cut it up into pieces small enough to fall down through the drum and into this crusher car beneath the drum. Here the pieces are broken down to a maximum dimension of 5 in. and fed into a sluice

With proper care in cutting the chunks can be eliminated, but it is easily possible to cut the coke faster than the crusher can handle it. The 18-in. grating added 2 ft. from the top of the crusher car hopper protects the rolls from damage should large chunks inadvertently fall from the drum. It also retains the chunks where they can be manually broken up. When the coke is moderately hard the time required from the beginning of the boring until the drum is completely clean averages about 6½ hrs. This corresponds to an overall coke removal rate of about 0.7 tons per min. Considering the time consumed in changing tools, inspecting the drum,

TABLE 3—Log of a Typical Drum Cycle

Elapsed Time Hours	Operation
0.0	Switch oil stream to clean drum. Steam full drum to bubble tower.
0.5	Stop steam to bubble tower, steam to blowdown.
0.75	Stop steaming, start cooling with water.
2.75	Stop cooling, start draining water, blinding and unheading.
4.0	Start decoking.
11.0	Finish decoking, start heading up and removing blinds.
12.5	Steam test.
13.0	Finish steam test.
18.0	Start heating.
24.0	Switch in oil stream from full drum.
48.0	Switch oil stream to clean drum.

etc., the maximum coke removal rate is probably in excess of one ton per min.

When the drum is completely clean the transfer line and condensate line are inspected and cleaned if necessary, the steam out valves are blasted with steam and the drum heads are replaced. After removing blinds and steam testing, the drum is ready for heating prior to another 24 hrs. of coking service.

Operations in Coke Storage Area

The coke-water slurry discharges onto an inclined chute, the bottom of which is made of 6-mesh steel screen. The majority of the coke rolls down the screen while the water, together with all material below about 20 mesh, passes through the screen and down a solid chute to a temporary settling pond, which is retained by a coke dike. A number of pipes are embedded in the dike and the water overflows through the pipes into a drainage ditch which leads to the secondary settling basin. The coke which rolls off the screen is moved by a bulldozer into piles from which it is loaded onto trucks.

This arrangement for separating the water from the coke is temporary and was devised after our original efforts along the following lines were unsuccessful. Originally it was planned that the coke would be piled in a circular dike of such proportions that the coke and water from one drum cleanout would be retained behind the dike. It was expected that the water would filter off promptly to permit moving the coke out of the way with a bulldozer to make room for the next cleanout. However, the quantity of water (about 1,500,000 gals.) and coke from one cleanout was so great that we had difficulty building a dike large enough to contain it. Furthermore, the fines content of the coke plugged the pores of the dike so that 3-4 days were required for the water to filter out.

A permanent coke-water separating installation is under consideration which consists of a screen chute, a series of hoppers which can be used for loading trucks, and a primary settling basin which can be easily cleaned of coke.

Presently, a loading crane is used to move the coke from the pile to the hauling trucks. The load is measured by weighing and delivered to the Great Lakes Carbon Corp.

To return to the water cycle, two 500,000-gal. secondary settling basins have been provided to permit the deposit removal from one while the other is in settling service. These basins are located at each end of a 3,000,000-gal. storage pond, into which they overflow through submerged pipes. The pipes are so located as to leave both the settled and floating fines in the secondary settling basin. The relatively clean water from the storage pond is returned to a surge tank in the unit area by two vertical deep-well pumps. The jet pumps, the drum cooling water pumps, the sluice water, and the automatic make-up water to the coke-slurry pump suction pit are all supplied from the surge tank.

Make-up water is supplied to the system from the Los Angeles Metropolitan Aqueduct System, or from the refinery wells. Tentative plans have been made to utilize the effluent water from the refinery waste water system for this purpose.

TABLE 4—Operating Conditions and Yields for Coking Unit

Operating Conditions	
Reduced crude charge, b/d	15,000
Furnace charge, b/ d	20,000
Recycle/fresh feed	0.33
Furnace outlet temp., °F.	920
Drum inlet temp., °F.	900
Drum outlet temp., °F.	830
Drum pressure, lbs.	56
Visc. of fresh feed, sec. SF/122	700
Yields	
Total gas, wt. %	14.0
Raw B-B, liq. vol., %	0.8
Debutanized gasoline, liq. vol., %	22.5
Light gas oil, liq. vol., %	36.5
Medium gas oil, liq. vol., %	16.7
Coke (by difference), wt. %	19.1

Operating Conditions, Yields

Presently the unit is charged with 700 sec/SF/122 straight-run residuum from Wilmington crude at a rate of 15,000 b/d, which effects a recycle to fresh feed ratio of 0.33/1. The 20,000 b/d charge to the furnaces is heated to 920° F.

The bubble tower is operated to produce gasoline with an endpoint of 380° F., light gas oil with an endpoint of 650° F., and medium gas oil as necessary to maintain a level in the bubble tower bottom reservoir. No heavy gas oil is being removed. In the stripper tower the gas oils are stripped to a flash point which makes them suitable for use as cutter stock, although at the present time the light gas oil is used as TCC charge. Tests are being made to test the feasibility of also using the heavier gas oil in TCC charge.

Under the above operating conditions yields were obtained as given in Table 4. Additional operating conditions have also been tabulated.

It is rather difficult to accurately determine coke yields. Because of varying coke density, measurements by coke drum levels do not appear to be too reliable. The above difference method includes in the coke yield any gains or losses in the process. The yields can be roughly checked by means of the weighed haulings which approximate 500 tons per day.

It is likewise difficult to obtain representative coke samples. Samples obtained show approximately 0.25% ash, 9% volatile matter, and a screen analysis satisfactory for its intended use.

As would be expected with this type of process, the high sulfur Wilmington residuum charge yields a gasoline with an appreciable sulfur content. This sulfur content and the olefinic content of the gasoline are sufficient to require sweetening and rerunning. Clear octane numbers in the neighborhood of 70 (motor method) are obtained with an octane spread of 8 or better. Lead susceptibility is fair and commensurate with the sulfur content.

Because of the desulfurizing characteristic of the TCC process, the coker gas oils have proven to be quite satisfactory as TCC charge stock despite their sulfur contents. The 650° F. endpoint light coker gas oil, when charged to the TCC units (bead catalyst) with a 1:1 recycle ratio, yielded 41% of 400° F. endpoint debutanized gasoline. Furthermore, an octane level of 79 M. M. clear and an octane spread of 10-12 points make this operation look quite attractive.

The low raw B-B yield is a result of the large gas yield from the bubble tower reflux accumulator which carries with it the bulk of the C_4 production. The total gas yield amounts to 8,000-9,000 Mcf/day. The dry gas after absorption amounts to some 7000 Mcf/day, which is just double the requirements at the coking unit furnaces. The excess 3,500 Mcf/day represents an appreciable contribution to the other refinery units' demands.

Effect of Operating Variables

Our operating time has been far too short to establish the effects of operating variables. Nevertheless, some indication of their effect has been obtained. Increased viscosity of the charge appears to shift the gasoline and gas oil production slightly toward more gas and coke. Furnace outlet temperature changes through the range 910-920° F. also had little effect on gas and gasoline yields; however, gas oil production increased with a decrease in coke yield. Reducing the recycle ratio shifted the yields from coke to the gas oil and lighter products.

From the above indications it appears that any benefit that may be derived from a high removal of straight-run gas oil from the charge is not appreciably invalidated by lowered coker yields. Yields may be varied extensively by manipulation of the recycle ratio and higher furnace outlet temperatures may be feasible.

Unit Flexibility

The unit is quite flexible in that it can be used either as a coker, a visbreaker, or any combination of these two. For any operation other than full coking a higher inlet to the coke drum would be used. The rate of residuum withdrawal from the bottom of the drum would determine the amount of coking permitted. In a full visbreaking operation, it is also possible to charge the fresh feed directly to the furnace along with the recycle. Under this arrangement, the residuum would be removed from the bubble tower bottom and the recycle from the bottom draw.

Automatic Purifier for Absorber Oil Adapted from Commercial Oil Heater

THE problem of keeping absorber oil clean can become a major expense item in the operation of a natural gasoline plant or gas recovery system. Dirt of all kinds, compressor oil and other impurities are picked up in the gas stream and contaminate the absorber oil. Since these products are usually not volatile they remain in the oil, increase its viscosity and end point, coat surfaces of heat exchange equipment and restrict flow through transfer lines.

Warren Petroleum Corp. has adapted a commercially obtainable oil heater, often used on leases in connection with gunbarrels and emulsion treaters, to automatic purification of absorber oil in several of its plants. The only expense, after installation, is for fuel gas and infrequent operator attention for periodic draining of "muck."

The device consists of a cylindrical vessel, mounted vertically. Near the bottom is located a bundle of hairpin tubes, connected to a stack and direct-fired with natural gas as shown in Fig. 1. Heat is maintained at the desired rate by a thermostat mounted opposite the tubes. The thermostat actuates a pilot valve, permitting natural gas to open a diaphragm valve also connected to the fuel gas supply; this in turn actuates the main-line diaphragm valve (throttling type) controlling fuel flow to the burner.

The unit is fed by a lean oil sidestream from the stripping still; quantity is controlled either with a liquid level controller or by a manually-operated throttling valve. The vaporized oil is taken overhead through a trap filled with crushed firebrick or similar material, which separates any entrained mist from the oil vapors. The purified oil then is condensed, cooled and retuned to the lean oil surge drum.

A manually-opeated drain is opened periodically to remove heavy ends accumulating in the heater. Frequency of draining depends entirely on the individual plant and extent of contaminating sources contacted by the oil.

In the latest installation of this device near Holliday, Texas, the purifier is 6 ft. in diameter by 7 ft. high. Temperature is maintained at 460-480° F. and approximately two to four gpm of hot lean oil is charged to the purifier. Since this is a new plant, contamination is quite low and the unit is drained but seldom.

Cost of the heater, according to the equipment manufacturer is approximately $660. It comes equipped with thermostatic control of fuel but does not include the mist extractor, which can be field-fabricated out of an old piece of pipe.

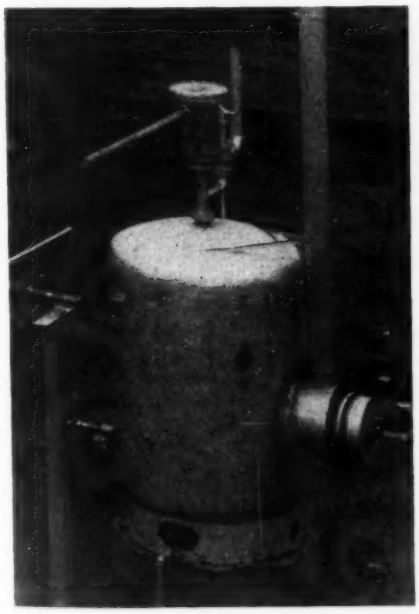


Photo courtesy J. F. Pritchard & Co.

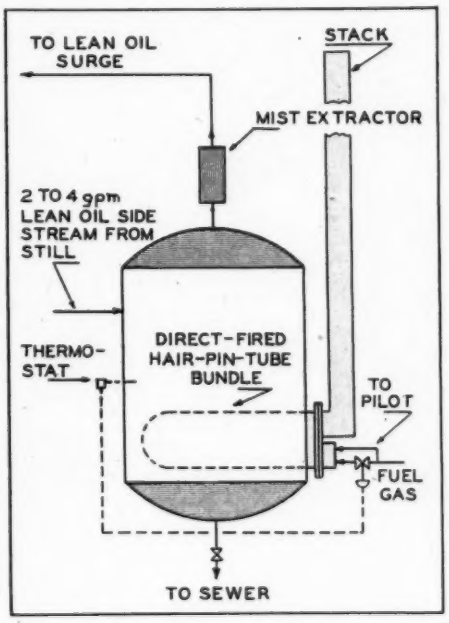


Fig. 1—Photo at left shows purifier for absorber oil adapted by Warren Petroleum Corp. from a commercially available oil heater. At right is a diagram of the unit. Oil is purified by vaporization, leaving "muck" behind for periodic disposal. Small vessel on top is a "mist extractor" made from an old piece of large diameter pipe and filled with crushed fire-brick. Small pipe on left side of purifier is the thermostatic control leading to the gas burner on the right side of the purifier

Drain Petcocks on Motor Casing Cut Failures from Dampness

EXPLOSION-PROOF motors are mandatory in many locations in most refineries. Republic Oil Refining Co., Texas City, Texas, has had particular trouble with water condensing in a transfer pump drive on intermittent service.

This motor, a 2300 v., 1750 r.p.m., 400 h.p., explosion-proof is located below ground level in a brick building whose walls frequently "sweat" in the damp Gulf Coast air. It has been out of service several times through coil-failure and, each time, has been found with the outer casing full of water to the ports although at no time has it been under water.

The motor, presently out of service due to a bent shaft, is being equipped with petcocks in the bottom of the outer casing at each end. Operators will be instructed hereafter to drain the motor before each time it is started to prevent water accumulating and possibly leaking through into the insulated windings. Unfortunately this motor cannot be run continuously, which would prevent moisture condensation in the casing.

DETROIT PUBLIC LIBRARY

Continuous Inspection Record Form Helps Minimize Forced Shutdowns in Refinery

ENGINEE
CONT

MARK	ITEM	SIZE	RUNNG. DATE	120 3-8-44	121 4-23-44	122 5-2-44	123 12-23-44
45	FURNACE TUBE	4" O.D.		3.22	3.23	3.25	3.27
46		4" O.D.		3.24	3.24	3.26	3.28
47		4" O.D.		3.22	3.24	3.28	3.30
48		4" O.D.		3.26	3.27	3.32	OUT ON LIMIT
49		4" O.D.		3.30	3.30	OUT ON LIMIT	3.18
50		4" O.D.		3.28	3.29	3.30	3.32
ETC.							
			TEST HOLE NUMBER				
	WATER WASH		1	16	16	15+	15+
	DRUM		2	16+	16+	16+	16+
	4' x 13'		3	17	17	16+	16+
			4	13+	13+	13+	13
1	NOZZLE	4"		24			24
2	VALVE	4"		20			20
3	TEE	4"		18			18
4	ELL	4"					
5	VALVE	4"					
6	TEE	4"			19		
7	VALVE	4"			19		
8	PIPE BEND	4"			10+		
9	PIPE BEND	4"					
10	TEE	4"					

Fig. 2—Continuous record form used in corrosion inspections. Actual full size is 11 x 27½ in. As indicated by shaded rectangles, furnace tube 48 was pulled out of service in Dec., 1944, because the I.D. had reached the limit for that particular tube. Correspondingly, tube 49 came off in May, 1944, for the same reason

TO LEARN how frequent inspections of equipment should be made and to minimize forced shutdowns because of corrosion, one large refinery has set up and maintains accurate continuous records, based on data from field inspection reports. An important and helpful feature of the system is the use of color identification code in the forms for type of material used.

A sample of the record form used is shown in Fig. 2. This record is kept in the Engineering Inspection Division office and field data is transferred to it at times of general or turnaround inspections.

Items are identified as follows: Furnace tubes by number and size, towers and drums as to test hole location, and piping as to number, type and size.

Field inspections are made by means of the field sketches shown in Figs. 3, 4, and 5. Copies of these field sketches are stapled to the appropriate sheet in the continuous record book for complete identification purposes.

The field inspector on each particular unit records the desired data for each item. The identifying number is stencilled on the part itself and corresponds to the number on the field sketch.

In the case of the furnace tube layout, Fig. 3, each tube is assigned a number. Test hole locations are shown on the water wash drum, Fig. 4. Each piping item in Fig. 5 is also assigned a number. Wherever possible, in the case of tubes

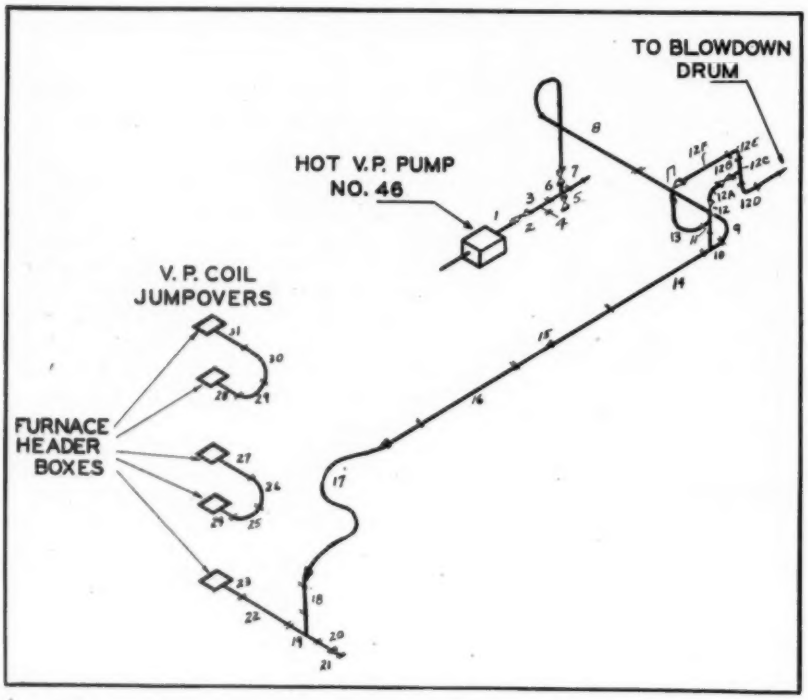


Fig. 3—Layout for pipe still furnace tubes, tower side. In this typical field sketch, each tube is assigned a number; however, for simplification only a few numbers are shown here. The numbers run consecutively in the direction of the flow

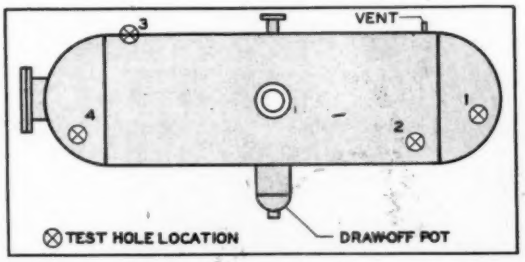


Fig. 4—Field sketch of wash drum, alkylation plant. Numbers indicate test hole locations. Test holes are placed so as to give data on each sheet and each head, and under both liquid and vapor phase conditions

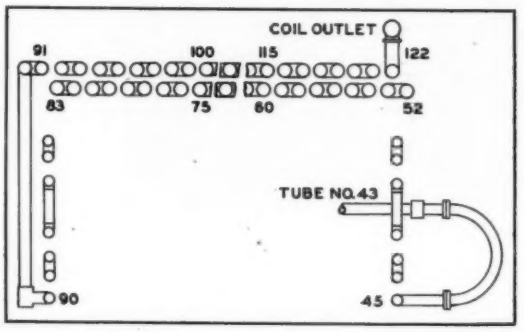


Fig. 5—Layout of vapor phase inlet piping. Each piping item is numbered consecutively in the direction of flow

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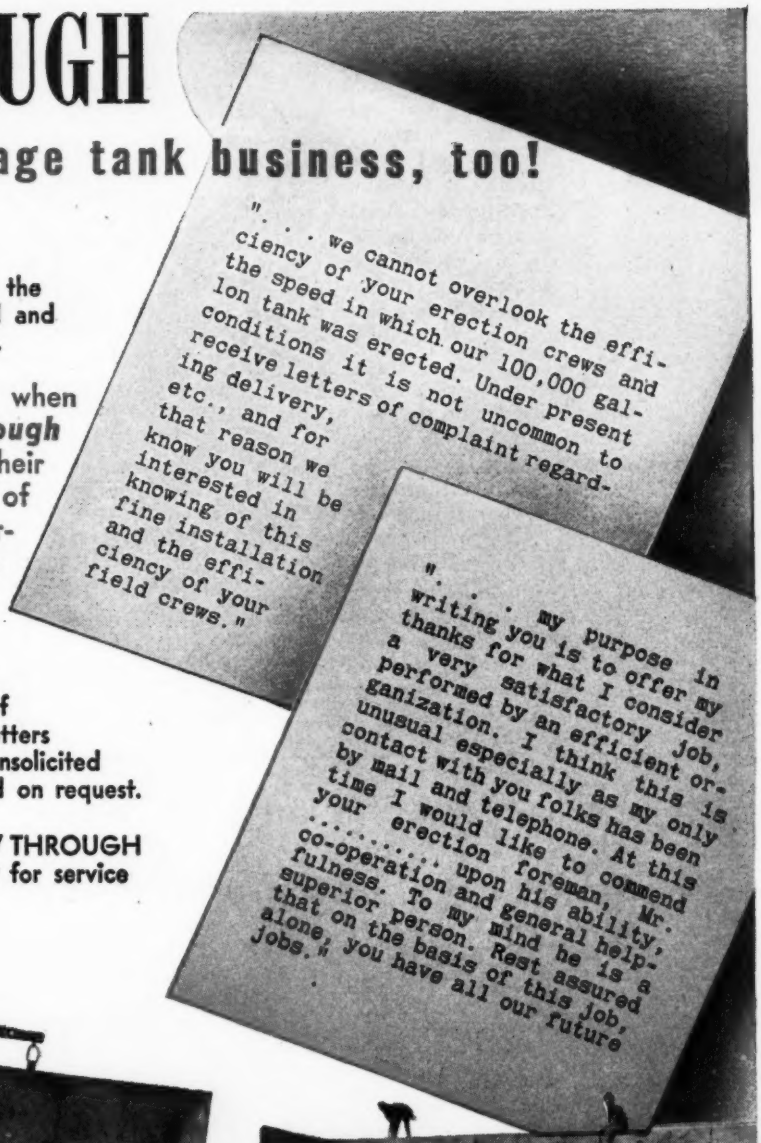
". . . we cannot overlook the efficiency of your erection crews and the speed in which our 100,000 gallon tank was erected. Under present conditions it is not uncommon to receive letters of complaint regarding delivery, etc., and for that reason we know you will be interested in knowing of this fine installation and the efficiency of your field crews."

". . . my purpose in writing you is to offer my thanks for what I consider a very satisfactory job, performed by an efficient organization. I think this is unusual especially as my only contact with you folks has been by mail and telephone. At this time I would like to commend your erection foreman, Mr. ..... upon his ability, co-operation and general helpfulness. To my mind he is a superior person. Rest assured that on the basis of this job, alone, you have all our future jobs."

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or piping, the numbers are arranged consecutively to correspond with the flow.

In the case of tubes, the data is inside diameter in hundredths of an inch. When the I.D. reaches a predetermined maximum, the item is replaced. In the cases of drums, towers, and piping, the determining data is thickness in thirty-seconds of an inch. When the thickness reaches a predetermined minimum, the part is replaced.

Test holes are placed in drums and towers, to obtain pertinent data on each sheet and each head, and to cover conditions under both liquid and vapor phases. Additional test holes may be drilled later where points of excessive corrosion are discovered.

So as to readily identify the types of ferrous and non-ferrous materials in service on any particular unit, a standard color scheme has been devised and is shown in Table 1. In actual practice, when a renewal of any item is made, the color corresponding to the type of material is blocked in the appropriate rectangle of the continuous record form with colored pencil. Subsequent measurements of this item are then recorded in the same color, except in the case of carbon steel. Since it is impractical to use yellow for this purpose, regular ink or black pencil is used.

TABLE 1 — Color Identification Code for Materials to be Inspected

(In actual practice, the color corresponding to the type of material is blocked in the appropriate rectangle of the record form shown in Fig. 2)

Material	Identification
Carbon Steel	Yellow
Carbon Moly	Green
DM-1-¼% Chromoloy	Blue
2% Chromoloy	Violet
2-½% Chromoloy	Red & Blue
4-6% Chromoloy	Red
9% Chrome 1-½% Moly	Yellow & Blue
11-13% Chrome	Green & Violet
KA2S (18-8 Stainless)	Brown
Silmo	Blue & Violet
Sicromo 2	Red & Green
Acrosil	Red & Yellow
Hastelloy	Green & Yellow
Admiralty	Orange
Antimonial Admiralty	Orange & Green
Red Brass	Orange & Violet
Arsenical Admiralty	Orange & Brown
Tellurium Lead	Green & Brown
Monel	Orange & Blue
Aluminum Bronze	Orange & Black
18-8 Moly	Brown & Violet
70-30 Cupro Nickel	Orange & Red

With the aid of this color scheme, it is possible to tell at a glance the type of material in service at any particular location. The use of such continuous records offers several advantages:

1. They enable the inspector to determine the frequency of inspection.
2. They provide a simple means of determining the corrosion rate.
3. Forecasts for replacement and repair of materials can be made with reasonable accuracy so that materials may be ordered in advance and be on hand when needed.
4. Knowing the corrosion rate, a basis is provided for economic justification of alloys of corrosion-resistant materials.

Loading Platform Efficiency Increased With Installation of Centrifugal Pumps

IN-LINE pumps which require no foundation and are an integral part of the line are used in the truck loading station at Republic Oil Refining Co.'s Texas City refinery.

The centrifugal pumps have been of particular advantage since they do not require loops and bends, and they are mounted on the pipe with simple flange connections instead of the conventional concrete foundation.

Trucks can pick up three grades of motor fuel; 100-octane gasoline, Diesel fuel and iso- and normal-butanes. Natural gas is available to purge tanks. Provision is made to load four or more tank trucks simultaneously. All pump controls and meters are located on the platform.

The pumps are piped to serve as circulating mixers as well as transfer pumps whenever desired. This arrangement also is shown in Fig. 6. When mixing, the operator closes the transfer-line valve and opens the jump-over valve, diverting pump discharge from the transfer to the fill-line, which is blocked to prevent discharge back to the blending house.

Only one objection has developed to the pumps since the new loading rack was commissioned. The pumps are silent and vibrationless. As a result they have been carelessly left running several times and damaged from excessive heat, since all lines were blocked. Consequently it has been necessary to install pilot lights on the loading platform to remind operators to turn them off when loading is completed.

Another advantage of these pumps according to company engineers is simplified maintenance. It is only slightly more difficult to remove the 165-lb. assembly from the line than to remove a spool or gate valve. Eight bolts take it off or put it on the line. Removal of eight more bolts gains access to the interior for maintenance.

Since the motor is totally enclosed (fluid pumped flows on all sides of the stator) it is drip, splash, and explosion proof, and is cooled by the liquid pumped. Hence it is located in this installation just outside the fire-wall surrounding bulk storage where it requires—and receives—little attention.

In the present installation these pumps handle only gasoline. The butanes and Diesel fuel are supplied from previously-existing facilities and simply transferred to the new loading rack, as shown in Fig. 6.

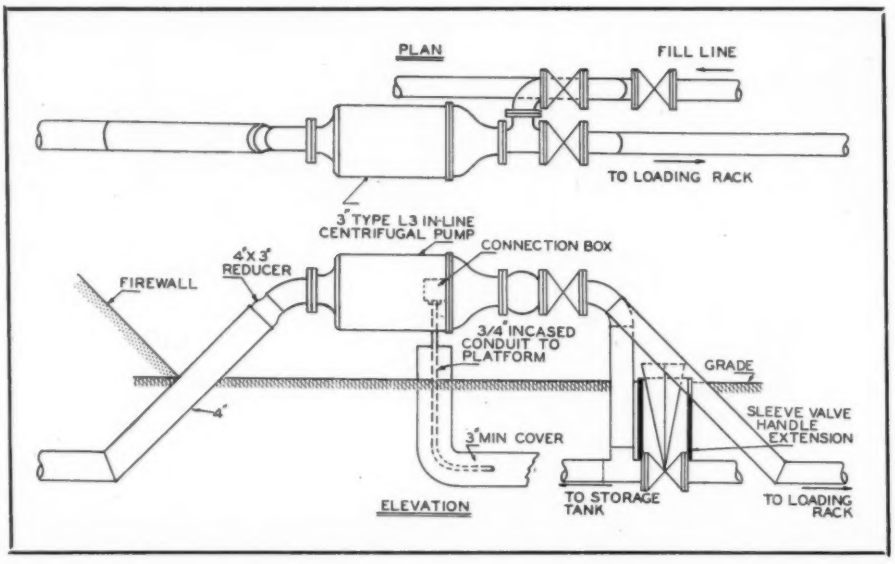
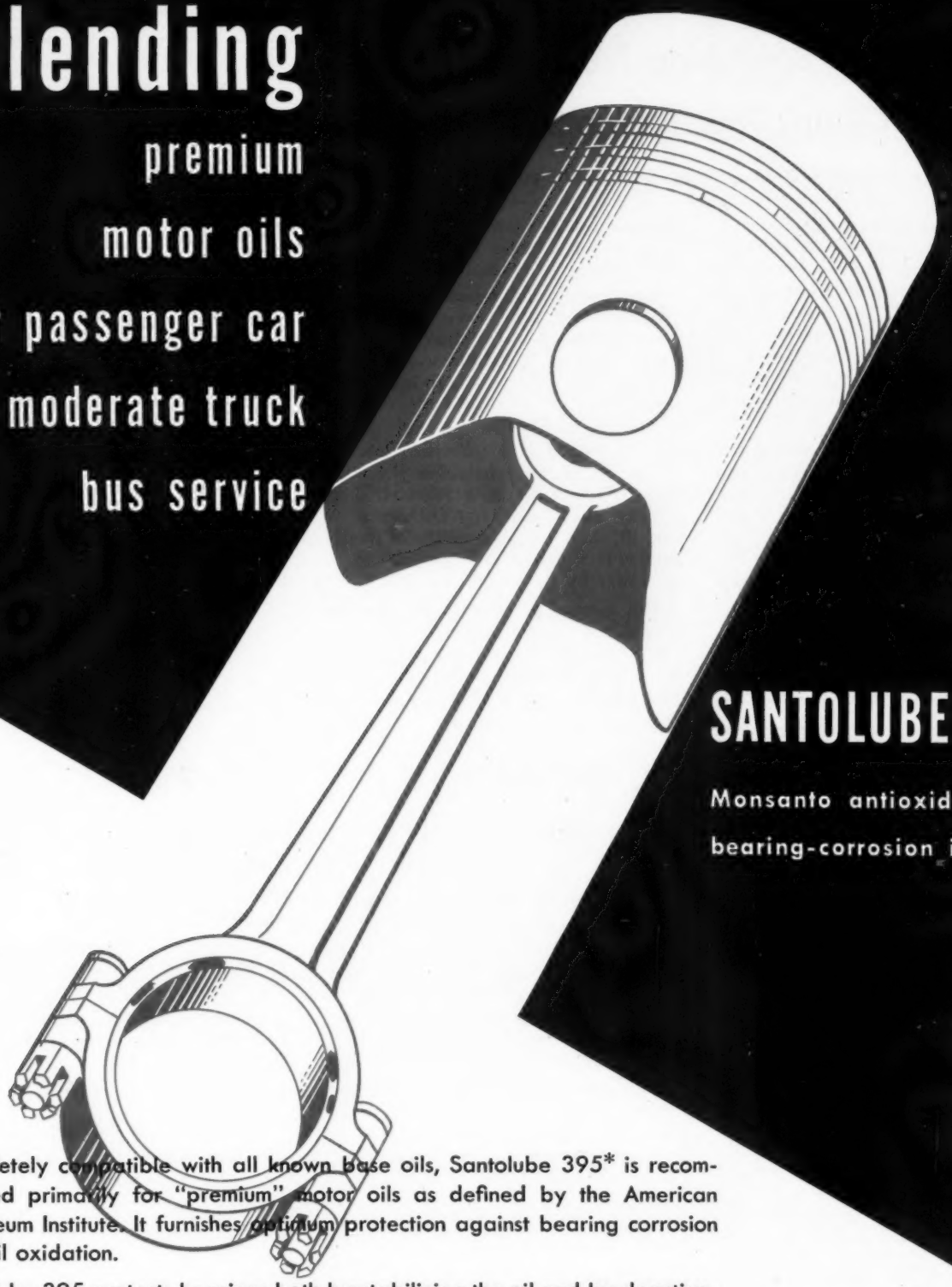


Fig. 6—Typical plan and elevation for installation of in-line centrifugal pumps, which serve both for circulation mixing and product transfer at Republic's truck loading station. Besides requiring no foundation for installation, these in-line pumps increase loading efficiency and simplify maintenance

blending

premium
motor oils
for passenger car
moderate truck
bus service



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Santolube 395 protects bearings both by stabilizing the oil and by deactivation of the metal bearing surfaces, rather than by coating the bearing surfaces with a protective chemical layer.

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*Reg. U. S. Pat. Off.

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Air and Water Scrubbing Treatment Effectively Cleans Fractionators

By RAY ELO, Process Supt., Sohio Petroleum Co.

AN AIR and water scrubbing treatment to loosen and remove scale and other dirt, following the usual steaming and flushing procedure for purging, has been found a simple but effective way for cleaning fractionating towers. The procedure was developed by John Weghorn, catalytic polymerization plant stillman at the Latonia Refinery of Sohio Petroleum Co.

After the tower has been flushed in the normal manner, the water is dropped below the top manhead, which is then opened up so that dirt to be removed can be flushed out without fouling the condensing system.

Compressed air is then admitted to the base of the tower through a gage or sight glass connection. Water is also turned on into the tower base at the same time. The air stream is kept on for several minutes and then turned off. Water continues to flow through the tower at all times, and after several minutes of overflowing the air is turned on again.

This procedure is repeated until water coming out of the tower is relatively clean and there are no signs of dirt still being removed. Then the water can be dropped out and the tower opened for inspection.

The cleaning action of this process can be explained as follows. When the air enters the tower it pushes the water through the trays at a relatively high velocity and a very high turbulence. As a result, considerable quantities of foreign matter is loosened and carried out of the tower by the water.

The system is effective in cleaning towers that contain catalyst and charcoal. Although it does not remove all dirt, it removes enough so that other cleaning operations are held to a minimum.

IDEAS—Wanted!

Plant operators, foremen, superintendents—Send in your own original contributions on "how we do it around our refinery". Possible subjects could include operating shortcuts, time and money-saving gadgets, repair ideas, inspection procedures, accident and fire prevention schemes — anything which has made your refinery more efficient, safer, and easier to run. Include photographs, drawings, or sketches, if available.

Material submitted for publication exclusively in Petroleum Processing is paid for at the usual space rates. The idea is the thing — we'll dress up the drawings and the written information. Send your contributions to:

Plant Practices Editor
PETROLEUM PROCESSING
1213 West Third St.,
Cleveland 13, Ohio

Machine for Cleaning Rust, Sediment From Tank Bottoms Built for $25

A TANK cleaning and buffing machine was invented by a tank foreman for Humble Pipe Line Co., at Longview, Texas, to replace hand-cleaning tank bottoms of rust and sediment. The machine can be built largely from scrap material, at a total cost of about $25, including labor.

The machine, built by Robert Hines, is illustrated in Fig. 7. It consists of a welded frame of angle iron carrying an air motor which was borrowed from a hand reamer to drive a large buffing brush. A small tail-wheel and a handle of convenient length completes the device. It occupies a space about two feet square and stands less than two feet high. The air motor can be removed in a few minutes for return to its regular job.

The buffing brush is made of a dozen 6-in. standard steel brushes, mounted on a steel rod which serves as a shaft. To one end of the rod is attached a 4-in. pulley, driven by V-belt from the 3-in. pulley on the motor. A steel strap, formed to fit the body of the motor or straight as preferred, is bolted to the frame to hold the motive power firmly, and a large U-bolt holds the motor down at its business end. The handle, of ¾-in. pipe, is made with a horizontal bar for convenience in handling the machine and on which to loop the air hose to keep it out of the way. It is welded to the carriage.

Company officials consider the machine does a better cleaning job than can be done by hand, and more quickly since it cleans a swath about a foot wide at each pass. The operator is not nearly so tired as when using the hand methods, does a better job more quickly than formerly. Because its weight is largely supported on the rapidly revolving brush in front, it shows up pits in the tank bottom that are not normally found without using chipping chisels. A much better bond between steel and primer is attained than was noted with hand-cleaning methods.

The machine is not intended or successful for removing asphalt, grease or hard scale from tank bottoms.

Submitting his idea in Humble's Coin-Your-Ideas program won inventor Robert Hines $200 in awards.

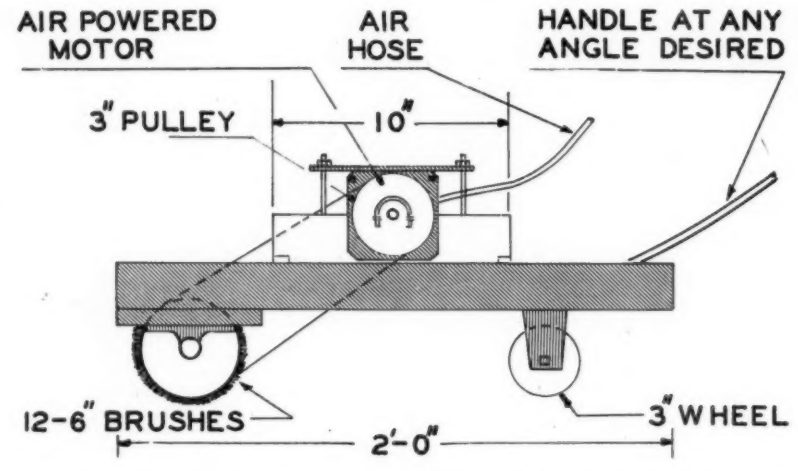


Fig. 7—Elevation view of tank cleaning machine, built largely from scrap for $25. The device uses an air motor to drive a steel buffing brush, and does a better job in less time in cleaning tank bottoms

UTOPIA—No Refinery Fires No Lost-Time Accidents

Sir Thomas Moore's account of the Mythical Island where the inhabitants lived in the enjoyment of social, political and industrial perfection, inspired this story

By F. J. SLUZE, Safety Director
Ashland Oil & Refining Co.

IS there a refinery with a perfect safety record?

No, of course there isn't in real life. The refinery in Utopia, however, being operated by Utopians, undoubtedly had a Safety Program which would go a long ways towards achieving the desired 100% safety record, if faithfully practiced, even in this land of hard realities.

So let's make an inspection of Utopia Refinery. Let's find out how they do it. We first examine the plant's accident record. It shows no accidents or fires during the entire history of its operations. "Unbelievable!" you say. Yes, but certainly not impossible.

Like most refinery inspectors, we start at the entrance gate. The guard on duty inspects us for badges, credentials, identification, and the like. Finding everything in order, he makes out our passes.

Utopians don't smoke in their refinery —except in the established smoking room, located safely away from hazards

As we enter the main gate, our attention is attracted to the main bulletin board. Notice that it is well posted, neat, not too crowded, well lighted, and kept immaculately clean.

Just inside the gate we see a sign reading "No Smoking Allowed Except in Smoking Room". We visit the established smoking room, and find it situated a safe distance from the operating area, and fire resistant in construction. Looking about the room, we see that receptacles have been provided for cigarette butts and pipe "dottle". An electric lighter has been furnished to discourage the carrying of matches.

Now we wend our way up the refinery road. We can't help noticing that the plant is neat and clean. Good housekeeping seems to be the first order of business—"a place for everything and everything in its place."

As a precaution against motor vehicle accidents, all employes walk on the left side of the road so they can face the oncoming traffic. Signs have been posted warning drivers of the speed limit and cautioning them to use their horns.

On our right is the material storage yard. We see that pipe is systematically and neatly stored according to size and kind. Each tier is snubbed to prevent rolling. Uniform sized boards are used to separate tiers. How *could* a man be hurt here?

A lot of inspecting still to be done, so we move on down the road to the carpenter shop. Here we find that new lumber is stored in bins according to size. Old lumber is stored in piles according to size—with all nails pulled out or bent down. Looking around the shop, we find that power saws are equipped with guards that protect the hands and fingers.

Back home we knew many an "expert" carpenter who has told us he couldn't possibly work with a guard on his saw, that he couldn't possibly turn out good work with a guard on his saw. We question one of the carpenters here at Utopia Refinery. "Doesn't stop me from turning out work to a perfection," he answers, "as a matter of fact, if I didn't use a guard, I'd soon have an accident. Then it *would* be impossible for me to turn out any kind of work."

We also find that the power saw guard is equipped with a safety dog that prevents lumber from kicking back while going through. Joiners and planers are also provided with guards. A container is on hand to collect sawdust and shavings.

Proceeding on our way through the refinery, we come across a gang of men digging out a concrete foundation. The man operating the jack hammer, as well as every other man in the vicinity, is wearing his goggles for protection against flying chips of concrete. From the look we get from one of them, we're glad we're wearing the lightweight goggles the refinery management lent us just before we began our inspection trip.

Next comes the machine shop. Here we find the lathes, drill presses, and work benches arranged in systematic, orderly fashion. Exit doors are clear of obstructions. Aisles are painted with bright lines to discourage disorderly placing of materials. The floor is clean and free of scraps, oil, grease, and water. Only tools in active use are in evidence; all other tools are in the tool room.

Non-spark tools are kept segregated from standard tools. Defective or condemned tools are kept in a special place for repairs or disposal. This prevents the tool room attendant from issuing them by mistake.

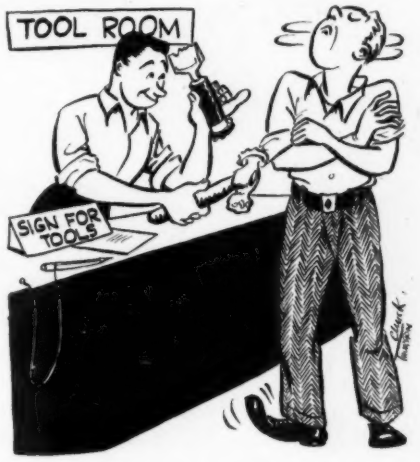
Oh! Oh! The man over there just spilled some oil (To ourselves we think "We knew this joint couldn't be perfect!) Our mistake, he fooled us. He immediately stopped and cleaned it up.

Notice that all machines are properly guarded to prevent fingers, hand, or arm being caught in moving parts. Notice also that all grinding wheels have a permanent glass shield to protect persons who are using the wheel.

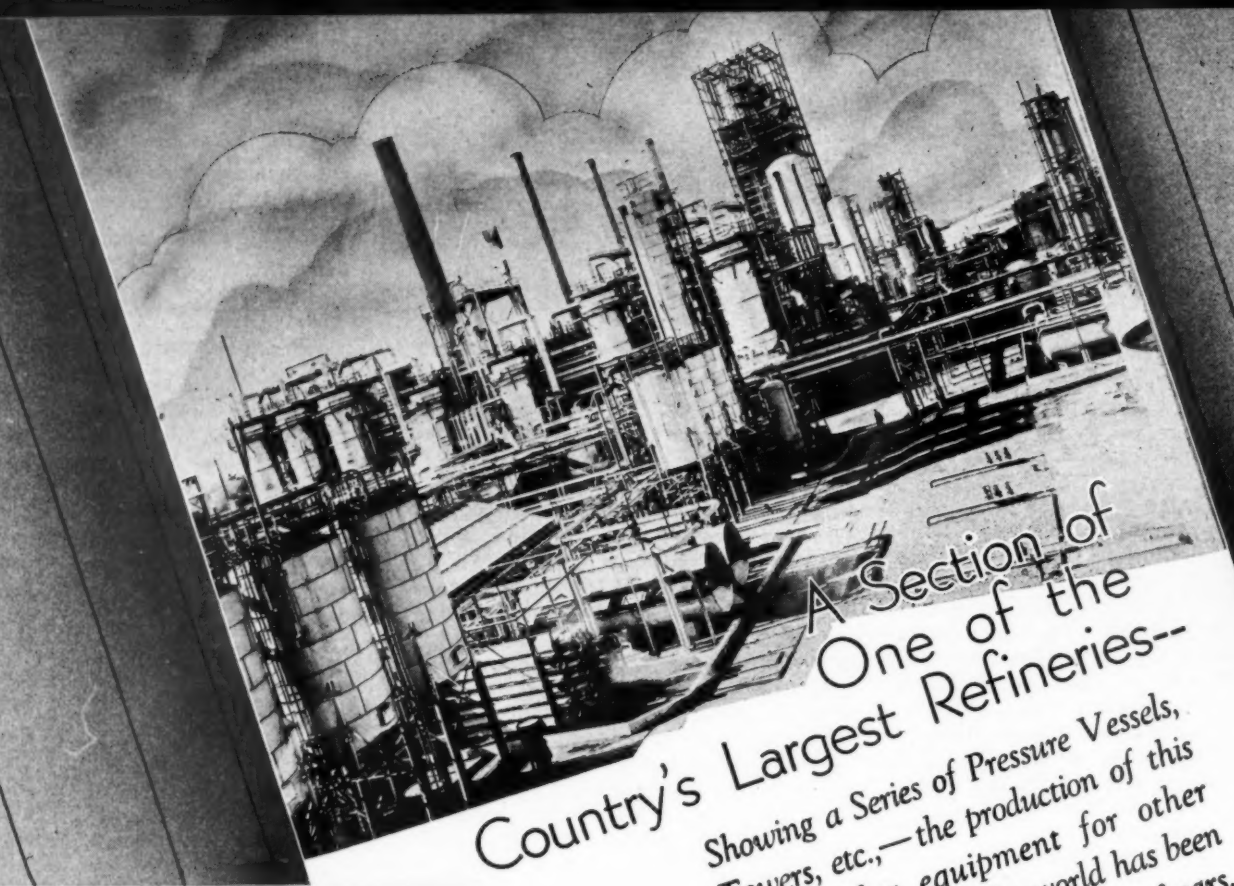
We now take a look inside the tool room. Let's examine some of the tools. All the hammers have proper faces, and the handles are securely wedged and have round, smooth surfaces. Chisel heads have been dressed to eliminate mushrooming, while the tool end is neatly sharpened.

There's a man at the window receiving some tools. Note that before he signs a slip for them, he inspects the tools for safe condition. Being satisfied as to their safety for his use, he accepts them and goes to his job.

Thus far our inspection trip has covered only a part of Utopia Refinery. In future issues we'll inspect conditions and practices of a specific nature, such as welding, pipefitting, tank cleaning, and cracking plant cleanouts.



If the tools offered Utopian maintenance man aren't safe, he doesn't take them. Unsafe tools cause accidents



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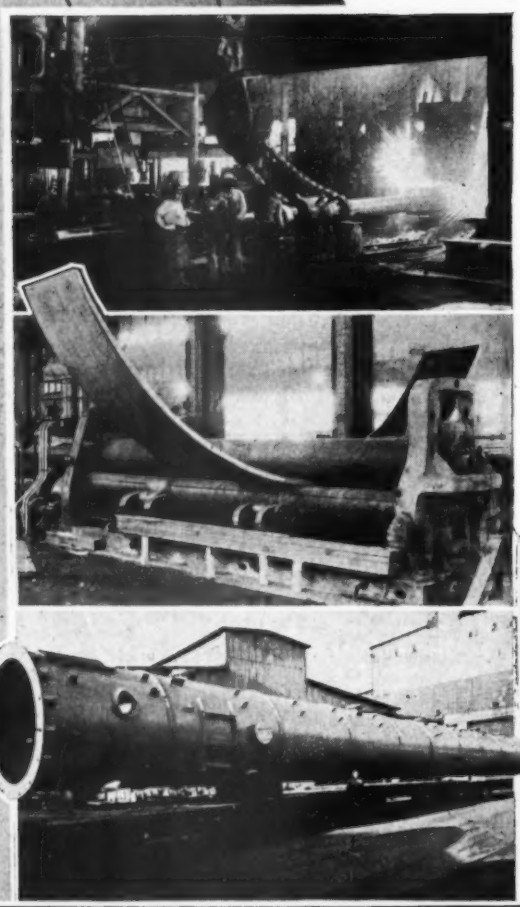

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Patent Trends in Petroleum Refining

By Peter J. Gaylor

Patent Attorney and Editor "The Technical Survey"

Developments disclosed in the patents reviewed below include:

A method for the removal of salt together with a substantial part of the water in crude as it comes from the well.

The use of unsaturated petroleum hydrocarbons as rubber extenders.

Preventing of foaming in alkali treating operations.

A method of producing larger amounts of amylenes from pyrolytic process.

Canadian process for producing trimethyl pentanes by alkylation of isobutane.

Oil Desalting and Dewatering

BY ADDING water and a suitable gas (usually propane) under pressure and then reducing the pressure, a removal of salt in crude oil as it comes from the well can be effected together with a substantial part of the water present in the oil. The addition of heat at suitable points and the use of a suitable alkali has been found to aid the removal. This method is described in Phillips Petroleum Co.'s U. S. patent 2,410,970.

A flowsheet of the process is illustrated in Fig. 1. Crude oil containing salt and water enters the system through pipe 1 and is raised in pressure by means of pump 2, after which it flows through heat exchanger 4 where it is heated, and then passes into mixer 6, after being blended with gas or vapor, coming in through line 7, and water containing caustic soda or other alkali, coming in from line 8.

Mixer 6 in a centrifugal pump which blends the oil and added materials into a fine mixture, although too fine a mixing has been found undesirable with certain crudes. Thereafter, the mixture is passed into heat exchanger 10 where it is heated to a still higher temperature. From this operation, the mixture is released into separator tank 12, where it is ejected through spray nozzles 17 into the water phase 16 heated higher with heating coils 13.

The pressure in separating tank 12 is reduced, so that gas and vapor are liberated during the spraying operation, resulting in the formation of three phases which separate and are drawn off separately, the gas through line 20, desalted crude oil through line 19, and aqueous layer off the bottom through line 18.

The amount of water added through line 8 is generally equal to the volume of oil treated, while the amount of alkali used with usual oils is about one pound per 16,000 pounds of oil. Propane is usually the gas supplied through line 7 at a rate of 5-100 lbs. per 300 lbs of oil.

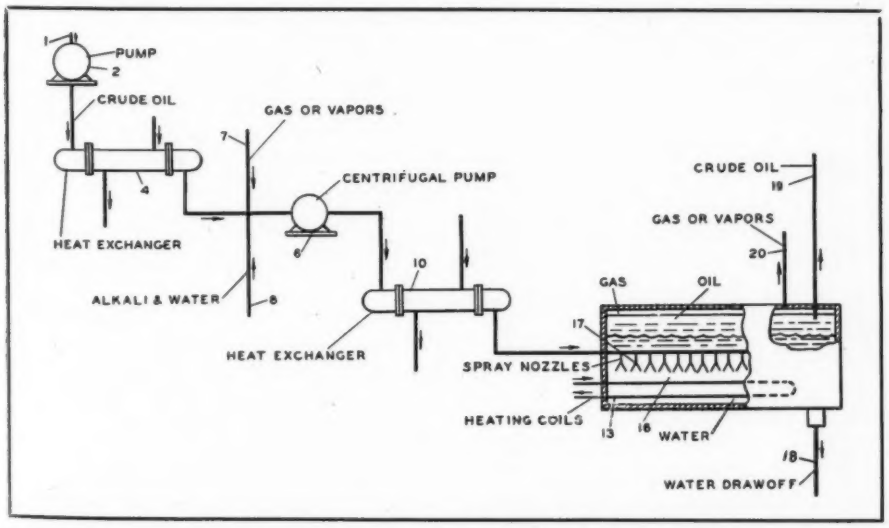


Fig. 1—Flowsheet for Phillips Petroleum Co. process (U. S. patent 2,410,970) for removing salt and water from crude oil by adding water and a gas under pressure and then reducing the pressure

Rubber Extenders

SOME unsaturated petroleum oils have the property of reacting with sulfur to give a vulcanized product resembling rubber, and such materials, known as "vulcanizable unsaturated hydrocarbon products", are milled in with rubber as rubber extenders.

DuPont has described, in its U. S. patent 2,410,839, the preparation of such unsaturated products containing about 90% carbon and 10% hydrogen, corresponding to the general formula $(C_3H_4)_n$, with molecular weights of about 300-1000, usually around 400. They have a reddish-brown color and are generally oils of high viscosity or resin-like substances at ordinary temperatures. Their specific gravities are usually greater than 1.0 and their boiling ranges are between 160°-380° C./12 mm. They also possess very low viscosity indices. Iodine numbers are usually low, below 60, and complete solubility in concentrated sulfuric acid is another characteristic.

These unsaturated hydrocarbons are generally associated with substantial amounts of paraffinic hydrocarbons, particularly in **lubricating oil extracts.** They are isolated by extracting the solvent extracts with a mixture of heptane and furfural, heating until all components are in solution, cooling until stratification occurs, and then drawing off the furfural layer containing the unsaturated hydrocarbons which are removed from the solvent by distillation.

Alkali Treating Hydrocarbons

THERE are many operations in the refinery in which alkali is employed, mainly for the removal of small quantities of weak acids or acidic compounds present. Caustic treating, solutizer extraction, extractive distillation and treatment with alkaline copper solutions are examples. In such cases, **foam and/or emulsions often occur which greatly reduce maximum throughput of the unit.** The nature of the substances responsible for the difficulties has not been definitely established, although it is believed that small amounts of impurities are responsible, such as compounds related to gasoline gums or similar resinous materials formed by the action of the components themselves or with the aid of oxygen.

Shell Development Co. in its U. S. patent 2,411,083, has found that the addition of a small amount of stable organic surface-active agent, having at

TABLE 1—Effect of Organic Surface-Active Agents in Reducing Foaming in Alkali Treating Operations

Organic surface-active agent	Conc. in gm./100 cc. solvent	Settling time in minutes	Vol. of residual rag	Remarks
Fresh solution	0	1½	0	No foam
Spent solution	0	35	9	Stable foam
I. Alcohols:				
Decyl alcohol	0.1	30	1	No foam } Act best as defoamers
Decyl alcohol	0.01	30	1	No foam
Decyl alcohol	0.0025	....	..	No foam
Lauryl alcohol	0.01	12	10	Light foam
2-ethyl hexanol	0.1	15	10	No foam
II. Amines:				
Lauryl amine	0.1	½	4	No foam
Amine ester of fatty acid	0.1	3	0	No foam
Amine ester of fatty acid	0.01	3½	0	No foam
Fatty acid salt of substituted oxazoline	0.1	3 2/3	0	No foam
Fatty acid salt of substituted oxazoline	0.01	3 1/3	0	No foam

least 8 carbon atoms per molecule and a molecular weight below about 600 and which is soluble or spontaneously dispersible colloidally in the treating solution, not only reduces foaming and gives improved separation, but also effects the breaking of the emulsions. These are preferably amines or alcohols having 8-14 carbon atoms.

Table 1 shows the results obtained with the use of such agents in spent aqueous copper ammonium acetate solution. The samples of the spent solution were subjected to an emulsion test in which they were agitated with an equal amount by volume of tertiary amylenes at 25° F. The resulting emulsion was allowed to settle and the time required for substantially complete separation was noted and whether or not at the end of the settling a residual rag (large globules of hydrocarbon surrounded by thin films of solution) was left at the interface between the solvent phase and the hydrocarbon phase. It will be observed that the alcohols acted best as defoamers.

Amylenes

IN THE alkylation and related fields, large quantities of highly concentrated olefins are required. In many cases the supplies of butenes are inadequate and use could be made of amylenes if they were available.

In its U. S. patent 2,409,815, Tide Water Associated Oil Co. discloses a method for producing larger amounts of amylenes from pyrolytic processes than are normally obtained, providing a C_5 fraction containing 60-80% amylenes.

The invention comprises subjecting *n*-hexane to pyrolytic decomposition at 1000°-1300° F. in presence of substantial amounts of propylene and ethylene. These olefins retard the production of ethylene and propylene and thus give greater yields of the higher olefins.

TABLE 2 — Comparison of Amylene Yields, Tide Water Process (U.S. 2,409,815) and Polymerization

	Process according to invention	Conventional thermal polymerization
Fresh charge, bbl./day:		
Propylene	600	600
Propane	200	200
N. hexane stock (145°-160° F.)	1,000	....
Total	1,800	800
Recycle stock, bbl./day:		
C_2 hydrocarbons	1,000	1,000
C_3 hydrocarbons	4,000	4,000
Total	5,000	5,000
Yields, bbl./day:		
Isobutane	30	25
Butylenes	125	50
N-butane	95	40
Isopentane	40	20
Amylenes	150	50
N-pentane	40	30
Other products	1,320	585
Total	1,800	800
Analysis of C_4 fraction, per cent:		
Isobutane	12.0	21.7
Butylenes	50.0	43.5
N-butane	38.0	34.8
Total	100.0	100.0
Analysis of C_5 fraction, per cent:		
Isopentane	17.4	20.0
Amylenes	65.2	50.0
N-pentane	17.4	30.0
Total	100.0	100.0

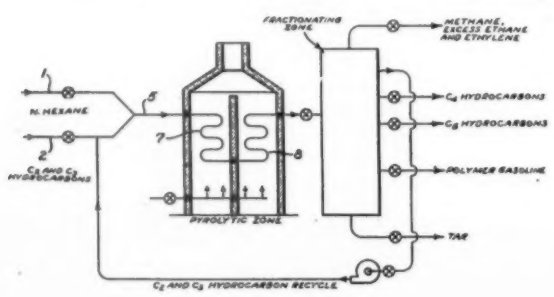


Fig. 2 — Flowsheet of Tide Water's thermal cracking process designed to produce high yields of amylenes (U. S. 2,409,815)

Fig. 2 shows a flowsheet of the process employed. *n*-Hexane is fed through line 1, while fresh C_2 and C_3 hydrocarbons are introduced through line 2, meeting recycle C_2 and C_3 hydrocarbons entering from line 5, whereupon the whole mixture enters coils 7 and 8 in the pyrolytic zone, after which the products are fractionated. A comparison of the results obtained with conventional thermal polymerization of C_2-C_3 hydrocarbons is shown in Table 2.

Other Hydrocarbon Conversion Developments

IN ITS Canadian Patent 427,587, Shell Development Co. covers a process for producing trimethyl pentanes by alkylation of isobutane with ethylene in presence of aluminum chloride catalyst and hydrogen halide at 10°-30° C. at which the 2,3-dimethyl-butane is the preponderant product, separating this from the higher boiling fraction, and reacting the 2,3-dimethyl-butane fraction with ethylene in presence of aluminum chloride.

Gulf Oil Corp. has described a method of cracking at high heat input rates without excessive coking by passing the hydrocarbon through a thermally insulated reactor in counterflow to a material of high electrical conductivity, the heating being done by the induction of electromagnetic currents in this material. (U. S. patent 2,406,640).

Selected Patents of the Month

U.S. 2,410,024 (Anglo-Iranian Oil Co.) — Isomerization.
U.S. 2,410,044 (Standard Oil Co. (Ohio)—Aromatization.
U.S. 2,410,070-2 & 107-8 (Socony)—Alkylation.
U.S. 2,410,074 (Hughes By-Prod. Coke Oven Corp.)—Thermal cracking and coking.
U.S. 2,410,096 (Socony)—Dioleyl ketone from oleic acid.
U.S. 2,410,111 & 51 (Univ. Oil Prods.)—Alkylating aromatics.
U.S. 2,410,166 (Sinclair Refining Co.)—Separating toluene.
U.S. 2,410,309 (Socony-Vacuum Oil Co.)—Continuous catalytic system.
U.S. 2,410,314 (Socony)—Preparing formed gels.
U.S. 2,410,316 (Univ. Oil Prods.)—Isomerizing —cracking.
U.S. 2,410,346 (Corning Glass Works)—(C_6H_5) RSiO lubricant.
U.S. 2,410,356 (DuPont)—Purifying TEL with peroxide.
U.S. 2,411,141-2 (Standard Oil Co. (Ind.) — Polyamine resins.
U.S. 2,411,150 & 78 (Standard Oil Dev. Co.)—Lubricating oil blends.
U.S. 2,411,153 (Socony)—Sulfo-phosphated oil.
U.S. 2,411,160 (Standard Oil (Ohio)—Oil containing phosphated cashew shell oil.
U.S. 2,411,186 (Hydrojet Corp.) — Releasing gases from liquids.
U.S. 2,411,200 (Pure Oil Co.)—Cracking in presence of brominated ester.
U.S. 2,411,211 (Phillips Petr. Co.)—Isomerizing butane.
U.S. 2,411,236 (Pure Oil Co.) — Converting hydrocarbons into organic sulfur compounds.
U.S. 2,411,256 (Phillips Petr. Co.)—Butadiene from acetylene and ethylene.

Continuous Catalyst Flow Achieved Without Using Vapor-Sealed Valves

In addition to the improved catalytic system described below, this month's review of new and improved devices used in petroleum processing and handling operations on which patents have recently been issued includes:

- **Two-coil fire thermostat uses calibrating adjustment**
- **New valve will handle fluids at temperatures up to 2600° F.**
- **Claim high aromatic yields in coking and cracking oven**
- **New heat exchanger design reduces tube sheet failures**

A CONTINUOUS catalytic system which does not require vapor sealed catalyst valves has been invented by three Socony-Vacuum men. The system is said to have less tendency to crush the catalyst, to have mechanical failure, or to cause variation of pressures within either reaction or regeneration zones.

Designed primarily for cracking operations, the method is equally adaptable to any similar catalytic hydrocarbon conversion process, such as naphtha reforming and the like.

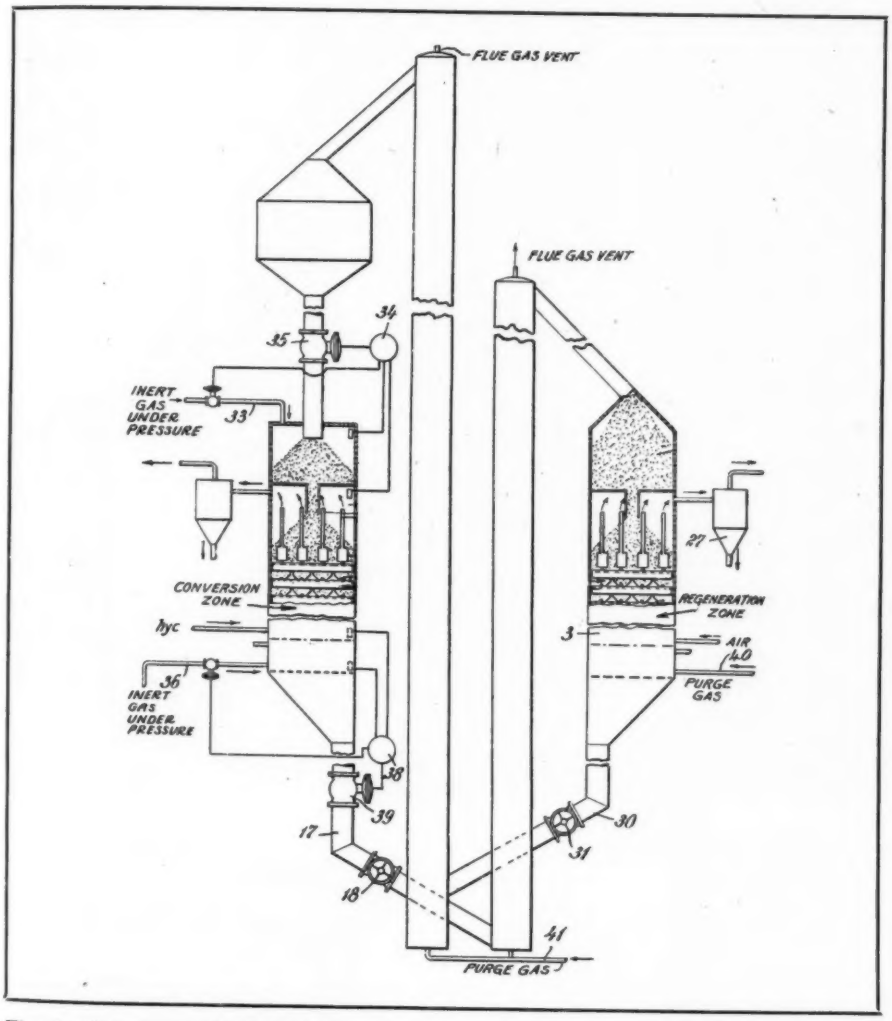


Fig. 1—Diagrammatic sketch of continuous catalytic system which does not require vapor-sealed valves (U. S. 2,410,309). Flow of catalyst through legs 17 and 30 is controlled so as to maintain closely-packed, freely-moving column of clay. Inert gas blankets provide additional seals in conversion zone of equipment

Seal is provided by controlling the flow and designing the height and cross-sectional area of the connecting legs so as to permit the free flow of catalyst at desired rates against pressure in the hoppers without the use of a valve. The flow of gas countercurrent to the clay will be negligible due to the enormous frictional resistance of the fine, closely-packed clay particles. An atmosphere of steam or inert gas is maintained in the hopper, further preventing the passage of any hydrocarbon vapors up through the clay legs.

It is pointed out that a more constant pressure is maintained in the conversion case by this system than where catalyst is being fed into the case and removed through vapor-sealed valves.

The system is shown in Fig. 1. Valves 18 and 31 may be either valves or orifices, and are used to regulate flow of catalyst in the two legs. Inert gas, which may be flue gas from regeneration case 3 instead of steam or any other inert gas, is fed at the points indicated by lines 33 and 36. Pressure differential controllers 34 and 38 regulate inert gas flow and catalyst flow at valves 35 and 39. Purge gas, for example flue gas from separator 27, may also be introduced to the regenerator zone through line 40, and to the catalyst elevators through line 41.

U. S. 2,410,309, issued Oct. 29, 1946, to Thomas P. Simpson, John W. Payne, and John A. Crowley, Jr., assignors to Socony-Vacuum Oil Co., Inc.

Two-Coil Fire Thermostat Uses Calibrating Adjustment

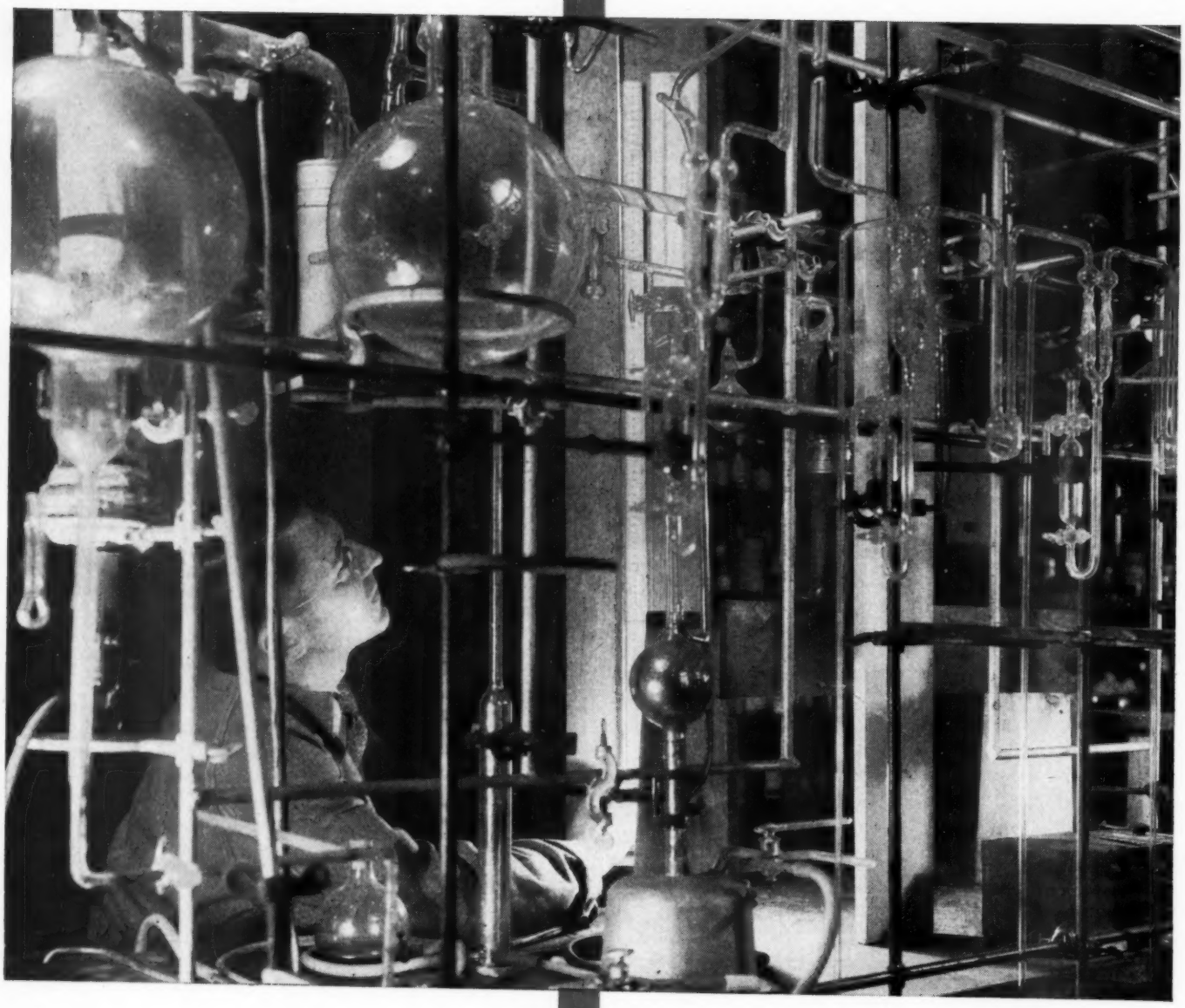
ADJUSTMENTS to correspond with changes in surrounding conditions can be made with a newly patented fire detecting thermostat of the rapid-rise-in-temperature type.

It is designed to be sensitive in detecting incipient outbreaks of fire under varying atmospheric conditions and can be adjusted by means of a calibrated dial to function with any desired minimum rapid rise in temperature.

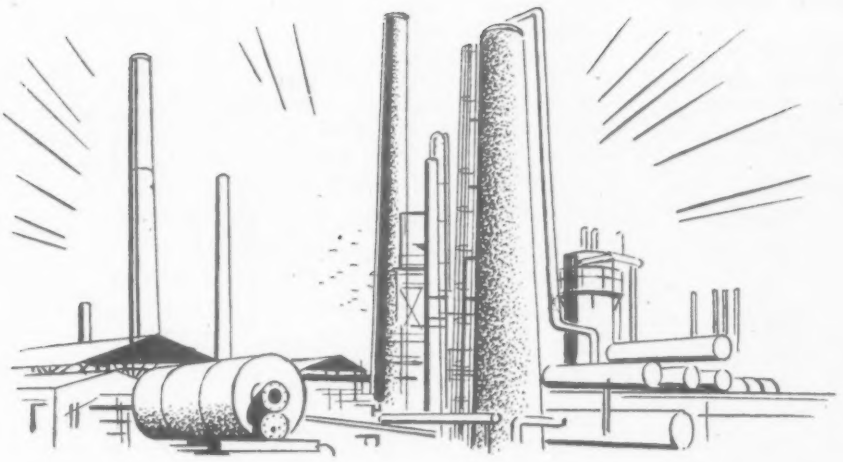
Close adjustment is made possible in its design by using two bimetallic helical coils, attached to the same rotating shaft, one exposed to the atmosphere and the other completely enclosed. The two coils are attached so that they exert their forces in opposite directions.

During a slow rise in temperature, the forces exerted by each coil are substantially equal and no movement of the

WORK



THAT'S NEVER COMPLETED



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shaft occurs. However, in the case of a rapid rise in temperature, the exposed coil is naturally affected first, and it therefore rotates the shaft, closing or opening a necessary electrical contact for energizing an alarm circuit.

U. S. 2,411,093, issued Nov. 12, 1946, to Ronald Purvis Jameson, Christchurch, New Zealand.

New Valve Will Handle Fluids At Temperatures up to 2600° F.

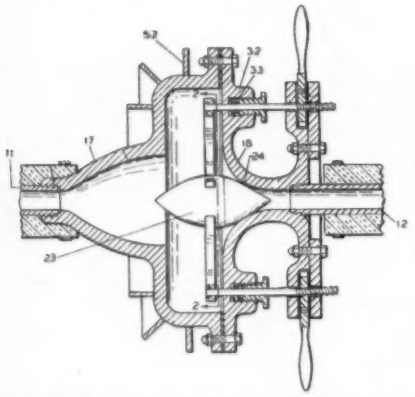


Fig. 2—High temperature valve useful for handling fluids from 600 to 2600° F. (U. S. 2,410,960). Streamlining the valve head 23, provision of cooling fins 52, and locating packing 32 and 33 in relatively cooler areas makes design of such valves possible

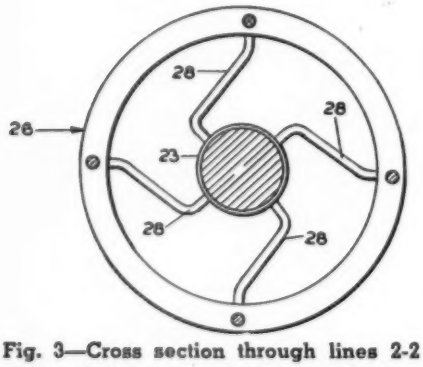


Fig. 3—Cross section through lines 2-2 of Fig. 2 showing construction of spider 26

High Temperature service; for example, handling fluids containing catalysts in refineries under temperatures of from 600 to 2600° F. and higher, is possible with a newly patented valve.

Said to provide streamlined flow and resistance to corrosion, the design of the valve cuts to a mininum the erosion of the valve seat from turbulent flow of hot fluid. Misalignment of the valve head because of temperature changes is also said to be eliminated.

Fig. 2 illustrates the valve in longitudinal cross section. The valve consists chiefly of casings 17 and 18, fastened together by bolts, and of valve head 23 mounted on a spider. Fluid flow may be from either direction, but is preferably from left to right, from pipe 11 through the valve to pipe 12.

Valve head 23, mounted on spider 26, is shown in Fig. 3, which is a cross-sectional view along line 2-2 of Fig. 2. The ess-bends of spokes 28 prevent misalignment of the valve head during temperature changes; expansion of the metal produces only a slight rotary movement of the valve head.

Packing rings and glands 32 and 33 are well away from the area of hot flow. Fins 52 on casing 17 serve to cool the fluid further. Additional fins may be provided, if desired, on casing 18.

Movement of the valve head in and out of seat 24 is effected by pinions 35 on studs 29. The pinions are rotated by teeth on ring gear 36, which is in turn revolved by handles 37. The invention also provides for othe methods of moving the spider.

U. S. 2,410,960, issued Nov. 12, 1946, to George B. Bunn, assignor to Phillips Petroleum Co.

Claim High Aromatic Yields In Coking and Cracking Oven

Straight Chain paraffinic petroleum hydrocarbons are converted into aromatics such as benzol, xylol, toluol, naphthalene and anthracene in a new design for a cracking and coking oven.

The oven is claimed to produce aromatics in good yield and high quality economically. In addition, the tar and carbon residue can be made into a high carbon coke suitable for carbon electrodes. Improvements in oven design, including a lower and upper heat treating chamber, devices for producing considerable turbulence in the vapors, and close control of flow and temperature are said to be the major effects in obtaining results claimed.

Good results can be obtained charging a low grade (8.5° API) cracked residuum oil at about 700° F., and continuously spraying it into the coking chamber, covering the hot floor. Vaporizing, as well as carbonizing, starts immediately. An 8-hr operating cycle is divided about as follows: Charging and coking—5½ hrs.; coking alone—1½ hrs.; calcining the residue—½ hr.; coke removal and burning off the carbon—½ hr.

The vapors produced during the on-stream period pass on to the cracking chamber and then to conventional fractionators separating out the aromatic conversion products.

U. S. 2,410,074, issued Oct. 29, 1946, to Charles H. Hughes, assignor to the Hughes By-Product Coke Oven Corp.

New Heat Exchanger Design Reduces Tube Sheet Failures

As a Means for reducing high temperature distortions and failures of tube sheets, a modified design of heat exchanger has been invented by an American Locomotive Co. engineer.

Adaptable to most heat exchangers, the invention is said to be particularly applicable to the type using hot fluid-catalyst mixture in the tubes and cold oil in the shell, and is designed to counteract the high temperatures usually occurring in the tube sheet.

In addition to the conventional baffles spaced throughout the length of the exchanger for directing the cold oil flow, the design provides a system of baffles at each end. These baffles cause the cold oil to flow at a designed rate close to the tube sheet for a greater length of time than in the conventional exchanger. A simplified design is shown in Fig. 4.

U. S. 2,411,097, issued Nov. 12, 1946, to Sigmund Kopp, assignor to the American Locomotive Co.

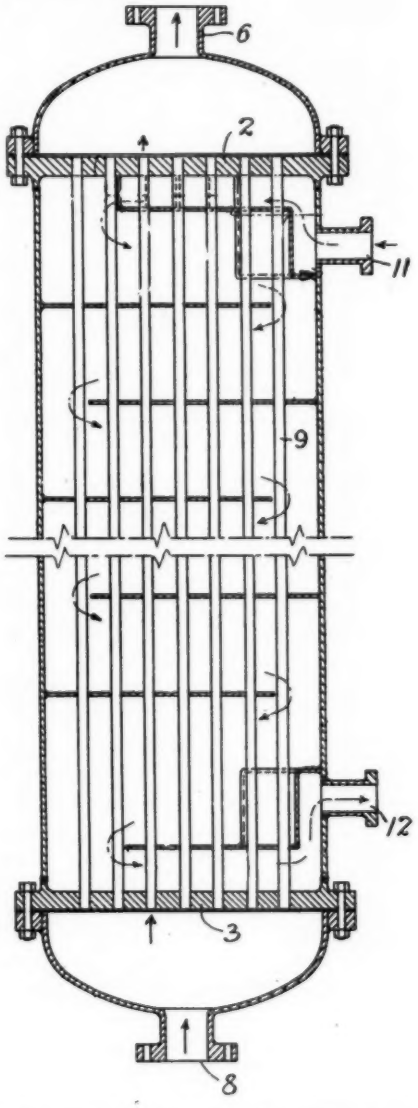


Fig. 4—Design of a simple vertical heat exchanger (U. S. 2,411,097), embodying additional baffles for increased cooling effect on tube sheets 2 and 3. Hot fluid-catalyst enters at 8, passes through tubes 9, and leaves at 6. Cold oil enters shell at 11, leaves at 12. Flow direction is indicated by arrows

Storm Run-Off in Open Sewers and Ditches Can Be Accurately Measured by Weirs

Article 13 in a Series—*By W. B. Hart*

In Charge of Waste Disposal for Atlantic Refining Co.

The principal forms of measuring devices for open sewers and ditches—rectangular suppressed weirs, rectangular contracted weirs, and V-notch or triangular weirs—are described, and formulas for calculations are given. All flow to be measured must pass through the measuring device for satisfactory results.

The percentage of rainfall on refinery property which is dissipated through other than storm run-off merits consideration. Such means of dissipation include infiltration, evaporation, and surface retention. The nature of the soil, degree of porosity, etc., and climatic conditions are factors which affect these functions.

STORM run-off waters may be controlled by various means, and the flow can be directed to proper points in the refinery through closed or open sewers, or ditches. The measurement of flow in closed sewers was described in last month's article.

Flow measurement in open sewers or ditches is a relatively simple matter. Weirs can be installed, and will provide a very satisfactory degree of accuracy. Because there are various forms of weirs, one or another will be adaptable to practically any form of ditch or open sewer, or, if sewers are large enough in diameter, can be used in sewer discharges. The principal weir forms are the rectangular suppressed weir, the rectangular contracted weir and the V-notch or triangular weir.

The installation of weirs, and the explanation of the necessary data and calculation can be presented rather briefly, but this brevity should not be taken as an indication of their relative importance in the estimation of run-off. Weirs probably are used more frequently as flow measuring devices than other appliances, even though their use for the purpose is based upon fundamentals which are complex. They have been studied extensively, however, and for practical purposes the equations developed are satisfactory as to accuracy when the weirs are installed properly.

The rectangular suppressed weir, and one method for its installation is shown in Fig. 1. If a head recorder is used in connection with the weir, averages for any period of time can be obtained and from these the rates of flow can be computed. The flow can be calculated by use of the equation:

$$Q = C\frac{2}{3}b\sqrt{2g}\ H^{3/2}$$

The constant C varies with the head on the weir and with the ratio of the head to the height of the weir. The formula developed by Rehboch[142] usually is accepted as the most reliable. This formula

$$C = \left(0.6035 + 0.0813\frac{H}{P} + \frac{0.000295}{P}\right)\left(1 + \frac{0.00361}{H}\right)^{3/2}$$

has been plotted for a number of conditions. The plot is shown as a part of Fig. 1. The symbol b indicates the breadth, or more properly the length of the weir.

Fig. 2 will explain the rectangular contracted weir. The clearance which must be allowed, so that free fall from the weir opening will not be affected, is important. A value of 0.62 for C will provide acceptable accuracy.

V-Notch Weirs

Low flows can be measured most conveniently with the V-notch or triangular weir, Fig. 3. This weir also is convenient for installation in the end of a sewer line. Calculation of flow makes use of the equation:

$$Q = C\frac{8}{15}\tan\alpha\sqrt{2g}\ H^{5/2}$$

The constant C has been determined by various experimenters. That determined by King will provide probably the greatest accuracy for the purpose of run-

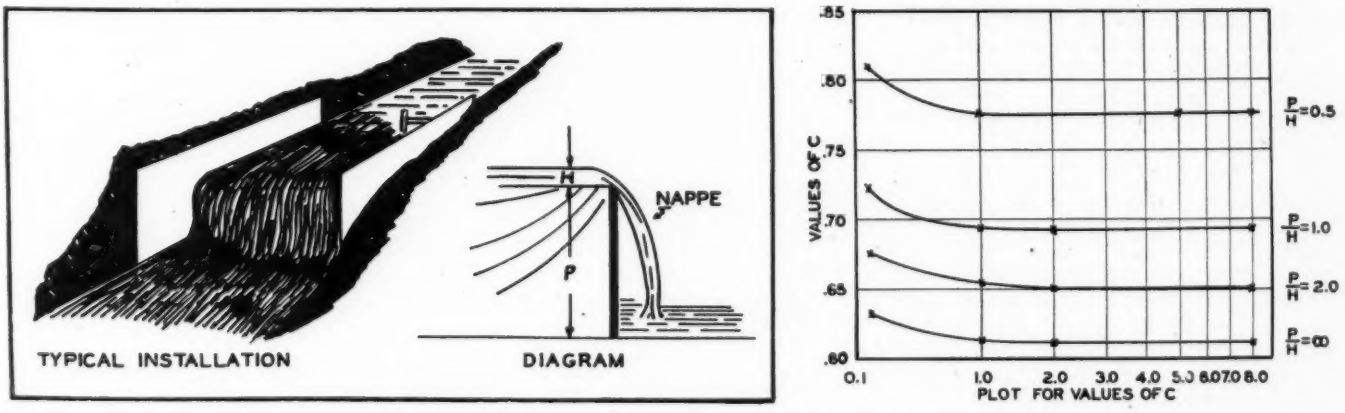


Fig. 1—Diagram and typical installation of rectangular suppressed weir. Graph gives values for constant C, at various P/H ratios where P is height of weir and H is height of crest above the weir

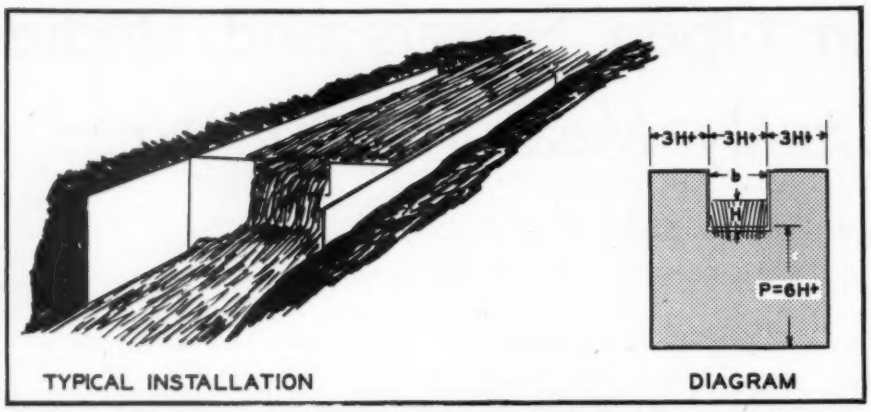


Fig. 2—Diagram and typical installation of a rectangular contracted weir

off measurement. This factor applies only when $\alpha = 45°$.

$$C = \frac{0.589}{H^{0.03}}$$

The three types of weirs mentioned above require that sufficient loss of head be permissible to allow the flow over the weir, commonly called the "nappe," to fall freely into space. This sometimes is not possible, particularly when the sewer system is flat. Under such circumstances the submerged weir should be used. This type of weir is shown in Fig. 4. The equation for the rate of discharge is the same as for other sharp crested weirs and is applicable for any of the types of discharge.

$$Q = C\frac{2}{3}b\sqrt{2g}\ H^{3/2}$$

The value of C has been studied exhaustively by Vennard and Weston[143]. They concluded that of the various analyses of flow over submerged weirs, that of Bazin is the most practical and useable. Values of C, based upon the relation of H_2 to H_1 and P to H_1 are tabulated in Fig. 4.

The Parshall flume, although not a weir, also makes possible relatively accurate measurement of flow without great loss of head. Indeed it is one of the desirable methods, and its application is illustrated in Fig. 5. The side walls of the flume are vertical and the line across the points where the converging side walls meet the throat is called the "crest." The floors slope as shown.

The head (i.e., depth of flow) is measured immediately along the side wall at a point two-thirds of the distance from the crest to the upper end of the inlet. When the depth of flow in the throat does not exceed 70% of H_a the following equations apply:

$$Q = 2.06H_a^{1.58}$$

(for a throat width of 6 inches)

$$Q = 4WH_a^{1.522W^{0.026}}$$

(for a throat width of 1 to 10 feet).

In which

W = the width of throat in feet.

All other symbols as already shown.

A simplified equation is as follows:

$$Q = 3.90WH_a^{1.58}$$

All Flow Must Pass Through Device

The very brief discussion of measuring devices which has been presented did not include certain important considerations which must be given careful attention when the device is installed. For example, it must be remembered that for the waste to be measured it must all pass through the measuring device. Therefore, no leakage around it can be permitted. Further, the velocity of the waste as it approaches the device must be relatively low. Thirdly, the orifice, weir, or other device must be identical with the type of device for

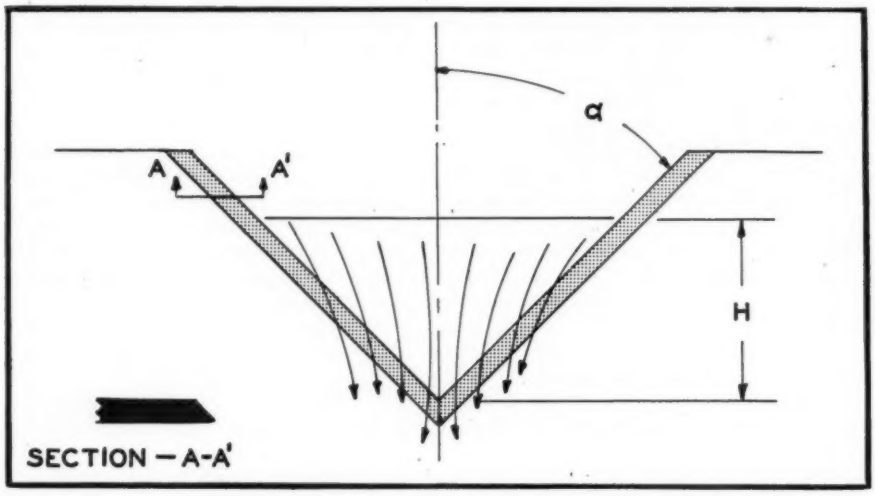
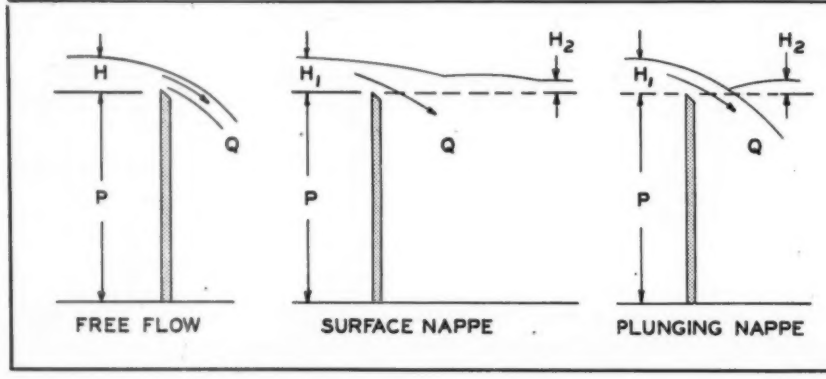


Fig. 3—Diagram of typical V-notch weir. Angle α is usually 45°. This type is usually used for low flows



H_2/H_1	P/H_1 8	P/H_1 4	P/H_1 2	P/H_1 1	P/H_1 0.5
0.95	0.322	0.326	0.402	0.449	0.502
0.90	0.456	0.497	0.540	0.589	0.640
0.80	0.611	0.650	0.694	0.737	0.783
0.70	0.700	0.740	0.781	0.821	0.866
0.60	0.771	0.808	0.845	0.883	0.925
0.50	0.827	0.861	0.895	0.930	0.968
0.40	0.876	0.906	0.936	0.967	0.999
0.30	0.920	0.947	0.970	0.998	1.023
0.20	0.957	0.980	1.000	1.022	1.044
0.10	0.991	1.010	1.025	1.043	1.060

Fig. 4—Submerged weir under three flow conditions: free, surface nappe, and plunging nappe. Table for values of constant C, for various ratios between height of weir and height of crest, and height of water on discharge side

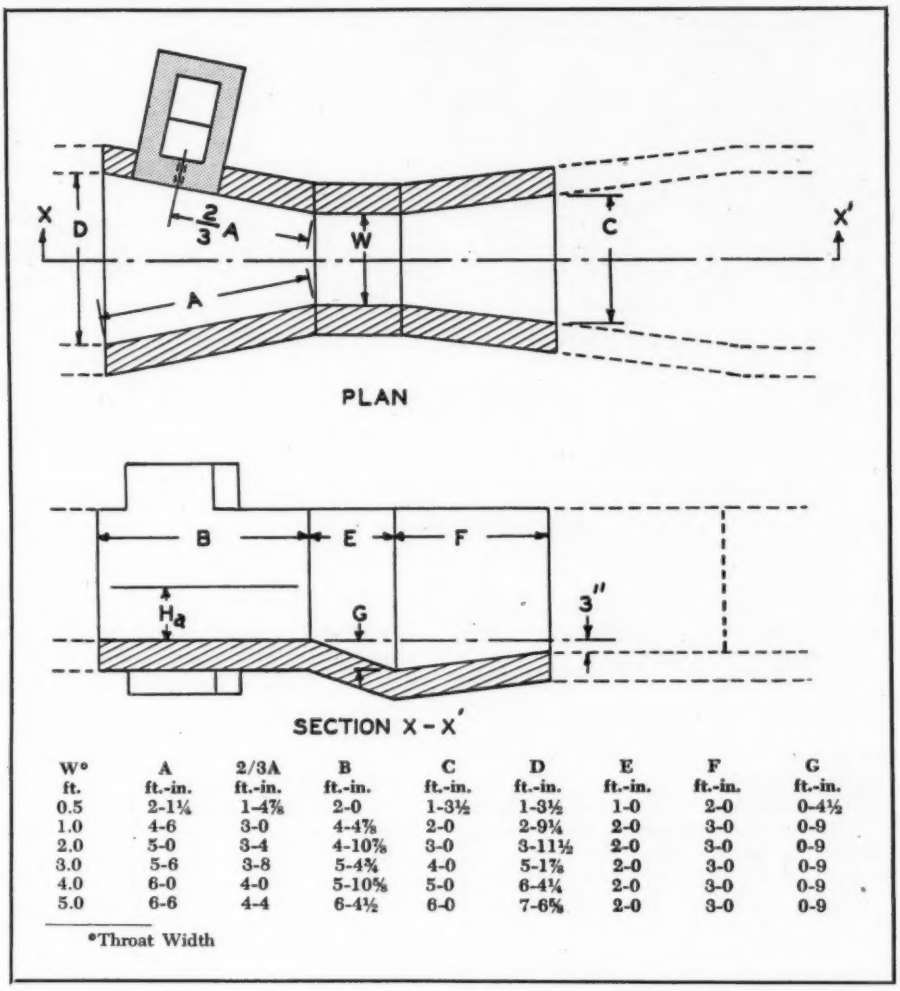
which the equations and coefficients given have been established.

The discussion of measuring devices has another purpose, and that is to emphasize the relatively simple ways by which the measurement of run-off, which is the most desirable method for determining this value, can be carried out. By measuring the dry weather flow from the area drained by a sewer system, and establishing this as a base, the rate of run-off during a storm can be established by similar measurement of the drainage flow during the storm. The rainfall can be measured with a rain gage.

Then a plot can be drawn as shown in Fig. 6. The relation of quantity to time can be established for both storm and dry weather flow. The difference will be the run-off. This can be related to the rain-fall rate and time in order to determine the extension of the run-off time beyond the time of cessation of the rain. Any treatment plant should be constructed so that it will have a capacity for handling the flow from the greatest storm experienced while measurements are being taken, provided this storm approaches in intensity that to be expected once in ten years.

There are other methods for determining sewer flows. Most of these depend upon a measurement of velocity at various points in the cross-section of the flow (i.e., a traverse), from which an average velocity is obtained and applied to the area of the cross-section. Velocity or current meters, Pitot tubes, Bentzil tubes, and similar devices are used in this way. But often the velocity in the sewers is so low that the accuracy of measurements by these methods is unsatisfactory.

Floats and substances in solution also



W* ft.	A ft.-in.	2/3A ft.-in.	B ft.-in.	C ft.-in.	D ft.-in.	E ft.-in.	F ft.-in.	G ft.-in.
0.5	2-1¼	1-4⅞	2-0	1-3½	1-3½	1-0	2-0	0-4½
1.0	4-6	3-0	4-4⅞	2-0	2-9¼	2-0	3-0	0-9
2.0	5-0	3-4	4-10⅞	3-0	3-11½	2-0	3-0	0-9
3.0	5-6	3-8	5-4¾	4-0	5-1⅞	2-0	3-0	0-9
4.0	6-0	4-0	5-10⅝	5-0	6-4¼	2-0	3-0	0-9
5.0	6-6	4-4	6-4½	6-0	7-6⅝	2-0	3-0	0-9

*Throat Width

Fig. 5—The Parshall flume, although not strictly in the weir classification, makes possible relatively accurate measurements of flow without great loss of head

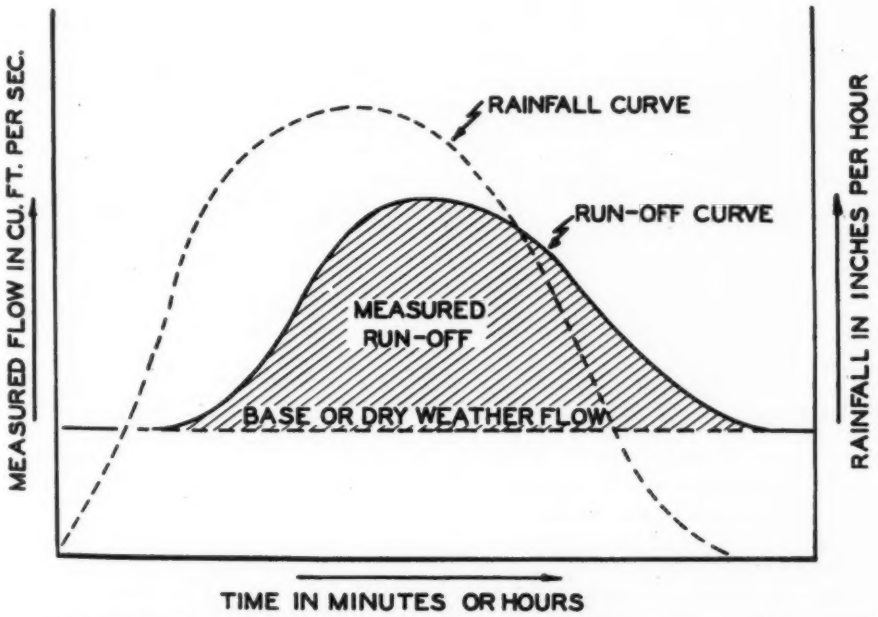

MEASURED FLOW IN CU. FT. PER SEC.
RAINFALL CURVE
RUN-OFF CURVE
MEASURED RUN-OFF
BASE OR DRY WEATHER FLOW
RAINFALL IN INCHES PER HOUR
TIME IN MINUTES OR HOURS

Fig. 6—Relation of measured run-off to dry-weather flow, and of run-off period to storm period

are used to measure velocity. For further discussion of all the measuring devices and procedures mentioned there should be reference to Vennard[144], Rouse[145], Liddell[146], King[147], Trans. A.S.C.E.[148], and others.

There will be many occasions when it will be necessary *to estimate* the rate at which run-off from rain will flow to some point of accumulation. Usually this will be the site at which a waste treatment plant is to be installed in perhaps a new refinery, or in one where waste treatment has not been practiced.

Estimation Is Difficult

Estimation of run-off is an extremely involved and difficult problem. There is an extensive literature on the subject, but this concerns large natural areas of timber and grass cover without structural development. To some extent small urban areas have been investigated, but even these are not comparable to refinery properties. Thus, the problem becomes one of adapting known procedures for estimating the run-off rate to the conditions which exist in the plant. Or, if the run-off from some section of the plant has

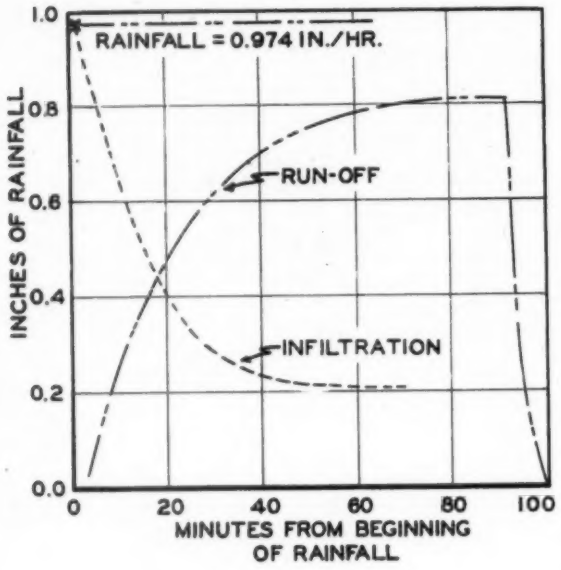


Fig. 7—Typical infiltration curve for the usual refinery soil. For a given rainfall rate, storm run-off increases as infiltration decreases

been measured, these data can be adapted and modified as an estimate for other sections similar in character.

It should be borne in mind that the total volume of the run-off is relatively unimportant. The rate of run-off is all-important, for treatment of waste usually is based upon rate.

When rain falls on the refinery property the water is dissipated in several ways. Important among these are infiltration, evaporation, and run-off. What is known variously as "surface reservoir capacity," "surface retention," "over-surface flow," and other similar terms, also plays an important role. As a general definition, these terms apply to the nature of the flow of the run-off to the point of accumulation, and how this flow may be retarded or accelerated by ground surface structures and the nature of the surface itself. Each of these factors must be considered and therefore will be discussed briefly. Volumes have been written on run-off flow, but only those parts of the literature which can be applied readily in refinery practice will be considered here.

Infiltration is concerned with that part of the rainfall which seeps into the soil and thereby is fixed. It may appear as subsurface flow later and may add to the flow of nearby surface waters. It even may reach the flow in open drainage ditches. But it will not be a part of the over-the-surface flow which makes up the important run-off resulting from the rain.

It will be obvious that water which falls upon paved (i.e., concrete, macadam, or similar paving) surfaces will not sink into them but will become surface flow in its entirety. Water which flows upon hard, frozen soil will penetrate such soil little if at all. A sun-baked clay soil also will be almost impervious but may be "sun cracked" in a manner which will permit some water to enter its structure.

But where the soil is sandy, or a sandy loam, or in other words is permeable, a considerable amount of water will penetrate. The soil has a saturation limit, however, which together with its permeability will act to reduce infiltration. This is because the permeability may not permit the water to be carried away rapidly through the deeper levels of its structure, and therefore the upper levels will become saturated more rapidly.

If the porosity of these upper levels is not great, saturation will occur even more rapidly, and leave more water in the form of surface run-off flow. For these reasons the nature of the soil must be known. Its usual degree of saturation (i.e., between rainfalls) must be known also, as well as the area which the soil represents. There is a rather similar pattern of infiltration which is represented as in Fig. 7. The figure assumes the usual low saturation of the soil at the start of the rainfall, an average permeability, and a saturation normal to a general clay-loam-sand soil often found in refineries.

Evaporation acts to reduce over-the-surface run-off flow but not greatly in most localities. However, all surfaces are wetted by rain and these "dry off" after the rain ceases. Also, any pools remaining after the rain has stopped usually disappear partly as a result of evaporation. Some water is retained by any vegetation present, and this also evaporates. Water returned to the atmosphere by transpiration, however, cannot be included.

In general it can be said that vegetation in the form a good stand of grass reduces both quantity and rate of run-off materially. Thus, although technically perhaps some of the items presented under evaporation really are matters of surface reservoir capacity, evaporation can play a small, but important role in the reduction of run-off.

Surface Retention Affects Run-off

Surface reservoir capacity, or surface retention, affects both the quantity and rate of run-off, particularly if the drainage ditch or sewer system of the refinery is included as a surface structure. Most refineries, particularly larger ones, have a more or less complete sewer system, and the tendency is to provide frequent inlets to the system so that wastes will be carried away promptly from any operation or locality. Therefore, insofar as surface run-off is concerned, the refinery automatically becomes divided into a series of areas, each of which is drained by a sewer inlet or several related inlets. This is so because once the flow has entered the sewers its movement toward the point of accumulation usually will be relatively direct and rapid. It is by the study of a variety of these areas, and by the summation of the run-offs estimated for each, that the run-off from the total area subject to contamination can be estimated.

There has been much thought given to making a choice between this method, which may be called a practical one, and the much more involved "unit hydrograph" method which has gained much favor among engineers in recent years. In each method assumptions must be made, and regardless of the accuracy of the complex computations based upon these assumptions, the results may be much in error, for there are not enough data from measured run-off from refinery properties to establish a uniform run-off pattern.

Next Month's Article

The runoff to the sewers will be that amount of rainfall which is not eliminated by infiltration, evaporation, or surface reservoir capacity. What percentage of the rainfall this may be under various conditions, how rainfall data can be obtained, and the application of the procedure to areas used as examples, will appear in the next article in February *Petroleum Processing*. The next article also will introduce the discussion on the treatment and disposal of wastes containing oil, either free or emulsified.

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(143)—"Submergence effect on sharp-crested weirs," John K. Vennard and Roy F. Weston, *Engineering News-Record*, June 3, 1943.

(144)—"Elementary fluid mechanics," John K. Vennard, New York, 351 pp, (1940)

(145)—"Fluid mechanics for hydraulic engineers," H. Rouse, New York, (1938)

(146)—"Stream gaging," W. A. Liddell, New York, (1927)

(147)—"Handbook of hydraulics," 2nd Ed., H. W. King, New York. (1929)

(148)—"Precise weir measurements," E. W. Schoder and K. B. Turner, *Trans., A.S.C.E.*, 93. (1929)

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Oil Company Synthetic Fuels and Lubes Show Good Records in Navy Tests

Synthetic fuel and lubricant products of American oil companies' long range research programs tested by the Navy at Annapolis gave satisfactory performance in gasoline and high-speed diesel automotive engines.

Included were The Texas Co.'s fuels from natural gas and synthetic ester lubricant blends; Union Oil Co.'s gasoline and diesel fuels from shale; Standard Oil Development Co.'s fuels from natural gas; and a synthetic lube made by Carbide and Carbon Chemical Corp.

Navy technologists and these oil companies cooperated with the editors of PETROLEUM PROCESSING in bringing the specifications and brief descriptions of the research projects together in this exclusive story.

SYNTHETIC fuels and lubricants already developed experimentally by oil companies in this country have given satisfactory performance in tests in gasoline and high-speed Diesel automotive engines.

These products of the oil companies' long-range research programs were used in demonstration tests conducted by the Navy at Annapolis June 13 in connection with conferences of the Army-Navy Petroleum Board and industry representatives to discuss the new technical problems of the armed forces. The synthetic fuels and lubricants were used in engines in standard amphibious craft, small boats and vehicles and in a turbo-jet engine at the Navy's experimental engineering laboratory.

The gasoline and Diesel engines powered and lubricated by synthetic products were put through performance tests which were described at the time by Navy technologists as "highly satisfactory". Liquid fuels made from coal by the Fischer-Tropsch process" gave true similarity of performance in the experimental gas turbine to Navy specification Diesel fuel under optimum operating conditions", it was stated. "In gasoline engines the 80-octane synthetic fuel was equal to or better than normal petroleum gasoline."

To confirm the satisfactory demonstration the Navy is planning further study both in the laboratory and in actual service. In another step in the study by this branch of the service of synthetic products, six type of Diesel fuels, including both synthetics and straight petroleum oils, are to be used in private industry tests. The six types which have been selected by the Navy's sub-committee on special fuel evaluation include:

Both 30 and 50 cetane number straight petroleum fuels; 87 cetane synthetic fuel obtained by the Navy in 1944 from France and manufactured by the synthesis of coal by the Fischer-Tropsch process; a 67 cetane number blend of Fischer-Tropsch liquid fuel and 50 cetane fuel from petroleum; a 50 cetane blend of Fischer-Tropsch fuel and 30 cetane petroleum product; a 50 cetane fuel composed of 30 cetane and 50 cetane petroleum products plus an additive.

Of the seven synthetic fuels used in the demonstration at Annapolis last June, one was a Diesel fuel made from coal in France by the Fischer-Tropsch process. One lubricant also was of foreign manufacture, a polyethylene oil manufactured in France. All the other synthetic products, however, were supplied by oil companies and one chemical manufacturing concern in this country, and were the results of the programs of study of synthetic substitutes for the natural products which these companies have carried on for some years. In the case of one company only were special products supplied only for the Annapolis demonstration. The supplying companies and the types of products are as follows:

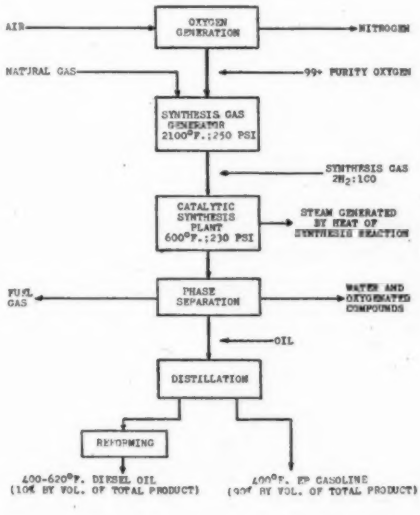

Fig. 1—Flow sheet for synthesis of various hydrocarbons from natural gas as developed by The Texas Co.

The Texas Co.—Gasoline and Diesel fuel made from natural gas; synthetic lubricating oil prepared by blending a highly refined mineral oil with an ester type synthetic oil of low viscosity.

Union Oil Co. of California—Gasoline made by retorting shale; Diesel fuel manufactured from shale.

Standard Oil Development Co.—Gasoline and Diesel fuel made from natural gas.

Carbide and Carbon Chemicals Corp.—Synthetic lubricating oil similar to an SAE 30 grade.

The above companies and the Navy technologists have cooperated with Petroleum Processing to supply specifications of the synthetic products used in the Annapolis demonstration and also brief descriptions of the research projects through which they were supplied. This data is given below:

The Texas Co.

The Texas Co. supplied a complete line of products including synthetic gasoline, synthetic Diesel fuel, synthetic lubricating oil and synthetic grease. The products were prepared by the development of the Fischer-Tropsch process as worked out in this country to use natural gas as raw material. The commercial development of this process, the recently announced "Hydrocol" Process(1) has led to the plans for the large scale units under construction at Brownsville, Texas, in which The Texas Co. with other oil companies is participating.

Actually a combination of processes is involved in the preparation of the synthetic fuels and lubricants by this development as shown in the flow sheet in Fig. 1. The steps are:

1—Preparation of high purity oxygen by low temperature fractionation of air.

2—Reaction of the high purity oxygen with natural gas (substantially all methane) to produce the desired

(1) "The New Hydrocol Process", by P. C. Keith, President, Hydrocarbon Research, Inc., National Petroleum News, *Technical Section*, July 3, 1946, pg. R-506.

TABLE 1—Properties of the Synthetic Gasoline Supplied by The Texas Co., for the Navy Tests.

Gravity, °API	63.8
Octane Number	
ASTM Clear	77.3
CFRR Clear	89.2
ASTM Distillation, °F.	
I. B. P.,	100
10%	136
50%	221
90%	343
E. P.	402
Doctor	Neg.
Sulfur, Lamp. %	0.005
Corrosion, CS @ 122° F.	Neg.
CD Gum, mg/100 ml	1
ASTM Gum. mg/100 ml	1
R. S. V. P. @ 100 °F.	8.0
Inhibitor, lb/1000 bbl	16 UOP 4
Olefins, %	76.7*
Aromates, %	None*
Carbon, %	85.4*
Hydrogen, %	14.6*

* Olefin percentage calculated from Bromine Number=118; aromatics, representative; carbon and hydrogen percentages calculated using MW = 104.

TABLE 2—Properties of the Synthetic Diesel Fuel Supplied by The Texas Co., for the Navy Tests.

Gravity, °API	38.0
Flash, P. M., °F.	162
Viscosity, SU @ 100 °F.	34
Cetane Number	42.9
Pour Point, °F.	+20
A. S. T. M. Distillation, °F.	
I. B. P.,	386
10%	440
50%	490
90%	545
E. P.	594
Color, N. P. A.	<3½
Cloud, °F.	cloudy at room Temp.
CS Corrosion @ 212° F.	Neg.
Carbon Res. (10% Resid.) %	0.25
Sulfur, Lamp, %	0.005
B. S. and W., %	Trace
Ash	None*
Aniline Point, °F.	123†
Diesel Index	46.7†
Carbon, %	85.0§
Hydrogen, %	15.0§

* Probable
† Representative
§ Calculated using MW = 199

TABLE 3—Characteristics of Synthetic Lubricating Oils Supplied by The Texas Co. for the Navy Tests.

Test	TL-964	TL-965
Gravity, °API	24.6	25.4
Flash, COC, °F.	460	450
SUV, 100°F.	303	286
SUV 210°F.	60.7	59.4
Viscosity Index	136.6	137.6
Color TR	3½	3¾
Pour Point, °F.	−10	−5
Carbon Residue, %	0.40	...
Neut. No. D-188	0.81	...
Ash	0.21	...

mixture of carbon monoxide and hydrogen

$$CH_4 + \tfrac{1}{2}O_2 \rightarrow CO + 2H_2$$

3—Reaction of carbon monoxide with hydrogen to produce hydrocarbon

$$n(CO + 2H_2) \rightarrow (CH_2)_n + nH_2O$$

4—Fractionation and finishing treatment are required to secure the desired products.

By varying the processing conditions it is possible to effect the production of hydrocarbons ranging from low molecular weight gases to high melting point waxes. Under the conditions employed in producing the material from which the gasoline and Diesel fuel were obtained, the overall hydrocarbon product consists of approximately 90% gasoline and 10% Diesel fuel. Worthwhile amounts of valuable chemicals are obtained as by-products.

Properties of the synthetic gasoline and Diesel fuel supplied for the Annapolis tests are given in Tables 1 and 2. With regard to the low cetane number of the Diesel fuel, the company stated that modification of the conditions of synthesis would result in a higher yield and quality for the Diesel fuel. Finishing treatment other than that employed in this particular case should result also in a substantially higher cetane number fuel. Modification of the conditions of synthesis would also change the gasoline quality and yield.

The synthetic lubricating oils, identified as TL-964 and TL-965, were prepared by blending a highly refined mineral oil with an ester type synthetic oil of low viscosity. In addition to providing "body" to the low viscosity ester, the inclusion of the mineral oil is regarded as desirable from the standpoint of its better "wetting" of metal surfaces, which it is believed provides better lubrication and greater protection against rusting. The ester type oil used in the preparation was prepared by the usual alcohol-acid reaction.

The particular synthetic oil employed in this blend has the obviously advantageous property of being completely miscible with mineral oil over a wide range of percentages, it is stated. In order to offset the somewhat higher viscosity-temperature susceptibility of the mineral oil in the blend, 2.5% of V.I. resins was added in each case. The oil TL-964 contained 4% by volume of the anti-oxidation and detergency additive. No such additive is present in TL-965, which is otherwise the same in composition. Pertinent tests on the two materials are given in Table 3:

The synthetic grease supplied by The Texas Co. for the Annapolis tests, the company stated, demonstrated a wider range of operating temperatures than any lubricant previously available. It is described as being particularly suited for aircraft use in that it will operate satisfactorily between a sub-zero tem-

perature of minus 65 and a high temperature of 250° F. This grease is made from 20% soap and a special synthetic oil. The following statement relative to this synthetic lubricating grease was made by The Texas Co.:

"During World War II a need was indicated for a grease for control bearings of aircraft, having much better low temperature characteristics than conventional greases. This resulted in Specification AN-G-3a, which had satisfactory low temperature characteristics down to about —65° F., which gave satisfactory service in aircraft control bearings at these low temperatures. However, it was found that under certain conditions elevated temperatures might exist which caused evaporation of the volatile components of the grease, resulting in some complaints on corrosion due to hardening and cracking of the grease.

"A need for a product having not only these good low temperature characteristics but also capable of lubricating satisfactorily at times at temperatures as high as 250° F. or more was therefore indicated. Texaco Uni-Temp Grease (TG-749) is not only satisfactory at the lower temperatures of —65 to —75° F., but also satisfactorily met the Navy High Temperature Performance Test of 1000 hours minimum at 250° F. and 10,000 rpm. It also operated satisfactorily for over 300 hours at 300° F.

"This product is a medium consistency grease containing approximately 20% soap and utilizing a special so-called synthetic oil of extremely high viscosity index (about 150). This combination of ingredients permits the product to easily meet the evaporation test of 23 hours at 210° F., showing only about 1.0% evaporation, whereas the former greases might show around 10%.

"Another interesting feature of Uni-Temp Grease is its extreme resistance to becoming softer on working down. For example, the original ASTM worked penetration on this grease is 286; that is, this is the penetration after 60 workings. However, even after 100,000 workings the penetration had only increased to 287.

"This ability to maintain its original consistency after long-time working is particularly advantageous in control bearings, as well as in instruments where working down of the grease may cause leakage and possible damage to other parts. Typical tests on this product in comparison with the new AN-G-25 Specification for grease, low temperature, low evaporation, lubricating, are given in Table 4."

The Texas Co. has been engaged in research on synthetic fuels and lubricants for more than 10 years and the products supplied for the Navy tests were obtained from materials resulting from projects which for some time have been a part of the company's general research program. The synthetic fuels were produced on several pilot units ranging in capacity from two to 10 b/d. The company also has a pilot unit for hydrocarbon synthesis at Montebello, Cal. with a capacity from 10 to 15 b/d of synthetic hydrocarbon. Fig. 2 is a photograph of a battery of units at the company's Beacon, N. Y., research laboratory now engaged in running hydrocarbon synthesis catalyst life tests.

Union Oil Co. of California

Gasoline and Diesel fuel manufactured from the retorting of oil shale were supplied for the Navy tests by the Union Oil Co. of California. This company's shale retorting and refining work has been carried on for several years and the fuels supplied were samples resulting from the regular pilot plant activities. The company has made the following statement concerning its shale oil fuels research project: Table 5 gives inspection data on the fuels supplied by this company for the Navy tests. Fig. 3 is a photograph of the pilot plant shale kiln.

"Our pilot plant retort is capable of

TABLE 4—Typical Tests on Synthetic Grease Supplied by The Texas Co., Compared with the new AN-G-25 Specification for Grease

Tests	AN-G-25 Specification for "Grease; Low Temp., Low Evap., Lubricating"	Texaco RCX-169 Uni-Temp. Grease (Formerly TG-749)
Penetration @ 77° F., unworked (ASTM)	.....	230
Penetration @ 77° F., worked (ASTM)	265-300	286
Working stability (AN-G-15) (100,000 stroke worker test)		
final penetration @ 77° F.	375 max.	287
Dropping point, °F. (ASTM)	325 min.	368
Lithium Soap, %	.....	20.6
Oil bleeding (50 hr. @ 212° F.) (AN-G-3a) (covered beaker) %	5.0 max.	2.95
Evaporation (23 hr. @ 210° F.) (CRC evaporation cell), %	3 max.	1.09
Corrosion (24 hr. @ 212° F.) (AN-G-3a)	No pitting, etching, or dark staining of strip. Slight brown stain is permitted.	negative
Dynamic water resistance test (AN-G-5a) % washed off (80° F.)	20 max.	12.5
Dirt count (AN-G-3a) particles 25 micron diam. or over	7500 max.	none
Norma-Hoffmann oxidation test (100 hr. @ 210° F.) lb. press. drop	5 max.	3
Low temp. torque test (3.0 g. chg.; 1000 g. cm.; —67° F.):		Clock-wise / Counter-Clockwise
Sec. rev. on original grease, max.	4 in either direction	2.0; 3.9 / 1.5; 4.7
Sec. rev. on 212° F. residue	.....	<1 / <1
High temp. performance (250° F.; 10,000 rpm) hrs. to failure	1000 min.	1000+*
Storage stability, pene. after 4 mos. @ 100-125° F., increase	30 max.	25 decrease
Aeration test (AN-G-15) (1 hr. @ 1000 rpm 77° F.) vol. inc., %	15 max.	none; ck.
Tests on oil component:		
Flash, C.O.C., °F.	.....	400
Viscosity, S.S.U., @ 100° F.	.....	71.8
Viscosity, S.S.U., @ 210° F.	.....	37.4
Viscosity index	.....	141
Pour point, °F.	.....	—50

* Basis two runs by outside laboratory.

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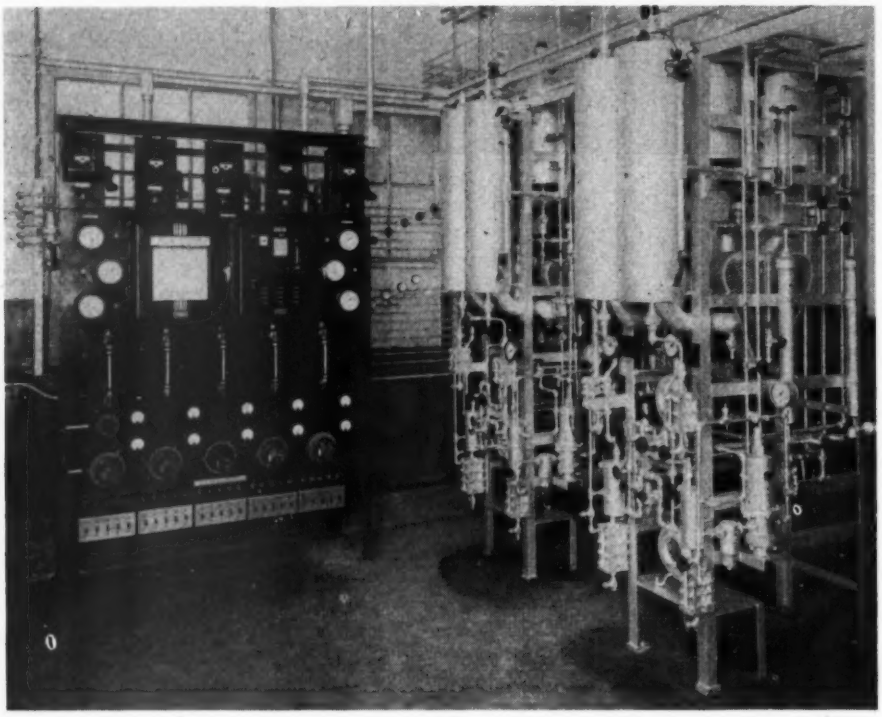

Fig. 2—The Texas Co. uses this battery of units in running hydrocarbon synthesis catalyst life tests at its Beacon, N. Y. research laboratories. Complete control panel for operation of the units is at the left

producing 1.8 barrels of oil per 24 hour day, based on Parachute Creek, Col. shale containing on the average approximately one barrel of oil per ton. We are designing a semi-commercial plant for an output of about 50 b/d. The process may be described as a continuous version of the old NTU process, in which heat for eduction is derived from burning a portion of the spent char through a downdraft system. No outside heat, power or facilities are required. The liquid yields consistently surpass conventional Bureau of Mines assay values. The essential development in this unit consists of a novel continuous underfeeding mechanism for introduction of shale which, for patent reasons, we prefer not to disclose in detail at this time.

"From the standpoint of product quality the most serious refining problem is the removal of nitrogen compounds, which cause instability on storage and engine difficulties, due to lacquering, ring-sticking, etc. Colorado shale oil contains roughly ten times as much nitrogen (mainly in the form of pyridine and quinoline derivatives) as typical California crudes, which are notably high in nitrogen.

"The samples furnished the Navy were refined by conventional acid-treating, but catalytic desulfurization and denitrogenation processes are undoubtedly in the picture from a long-term standpoint."

Standard Oil Co. (New Jersey)

The synthetic gasoline and Diesel fuel supplied by the Standard Oil Co. (New Jersey) for the Army-Navy Petroleum Board tests at Annapolis June 13 were produced in its 10 b/d experimental synthetic oil plant at Baton Rouge, La. The products were made particularly for the Navy tests. While the pilot plant regularly turns out synthetic fuels in small amounts the fuels are not normally finished to Army-Navy specifications, as was the case in this instance.

The experimental plant at Baton Rouge is comparatively new, although the work on synthetic fuels has been carried on by this company for many years and has now been taken up again after being discontinued during the war in favor of more urgent research. The process employed in making synthetic products is the modified Fischer-Tropsch, using natural gas as raw material, and employing the fluid catalyst technique which was developed and is applied commercially in the Fluid process for catalytically cracking petroleum stocks.

By the use of catalyst in fluidized beds, similar in principle to that for catalytic cracking, it has been found possible to greatly reduce the amount of cooling surface required to remove the heat evolved in the synthesis step. This makes possible a large reduction in plant investment along with a large reduction in maintenance and operating cost.

This company started research on the

TABLE 5—Inspection Data on Shale Oil Gasoline and Shale Oil Diesel Fuel Supplied by the Union Oil Co., of California for the Navy Tests.

	Shale Oil Gasoline	Shale Oil Diesel Fuel
Grav., ° API at 60° F.	48.2	34.6
Color	20+	Dark, clear
Flash, P-M, ° F.	...	190
Fire, ° F.	...	215
Viscosity, Say. Univ. sec. at 100° F.	...	36
Viscosity, Say. Furol sec. at 122° F.	...	...
at 210° F.	...	...
BS&W	...	...
Water by distillation	...	...
Pour point, ° F.	...	—10
Induction time, min.	1500+	...
Carbon residue, %	...	0.02
Ash	...	...
Sulfur, bomb, %	0.97(lamp)	0.96
Nitrogen, Dumas, %	0.153 (Kjeldahl)	0.52
Cetane No.	...	44.3
Octane No., Motor, clear	45.5	...
Motor+3 ml. lead	56.0	...
Research, clear	47.0	...
Research+3 ml. lead	58.0	...
Distillation, ° F.		
Init.	249	320
10%	294	442
30%	312	484
50%	330	514
70%	345	550
90%	363	594
95%	370	614
End point	384	621
Rec., %	98	97

Fischer-Tropsch process, particularly on the study of catalysts, soon after the synthesis was found to be possible by Fischer and Tropsch at the Kaiser Wilhelm Institute in 1925. More active research followed the acquisition of the technique and patent rights by Hydrocarbon Synthesis Corp., from Ruhrchemie, in 1938. Table 6 gives the properties of the synthetic gasoline supplied for the Navy tests, and Table 7 the properties of the synthetic Diesel Fuel. Fig. 4 is a photograph of the experimental synthetic oil plant at Baton Rouge.

Carbide and Carbon Chem. Corp.

The synthetic lubricant supplied for the Navy's demonstrations by Carbide and Carbon Chemicals Corp. was its "Unocon" LB-300 motor oil, which is described as approximately equivalent to an SAE 30 mineral oil. These lubricants are synthesized from natural gas or other hydrocarbon gases. The chemical nature

TABLE 6—Properties of Finished Synthetic Gasoline Supplied by Standard Oil Co. (N. J.) for the Navy Tests.

	Gasoline to Navy	Army Spec. 2-103B
Color—Saybolt	(Red)	Red
Sulfur—Wt. % (Turb.)	Trace	0.25 Max.
Doctor Test	Pass	Must Pass
Cu Strip Corr.—3 Hrs. at 122° F.	Pass	Must Pass
Olefins (Est.)—Vol. %	85-92	....
Aromatics (Est.)—Vol. %	1.7	....
Carbon—Wt. %	85.9	....
Hydrogen—Wt. %	13.9	....
ASTM Gum	Nil	4 Max.
Copper Dish Gum	4	....
ASTM Breakdown—Min.	480	480 Min.
Inhibitor Analysis—lb. UOP No. 5/1000 gal.	0.8	0.119 to 0.83
TEL Analysis—ml./gal.	1.95	3.0 Max.
ASTM Octane No.	81.6	80.0 Min.
Reid Vapor Pressure—lb./sq. in.	7.2	8.0 Max.
Gravity, ° API	64.4	....
Distillation:		
% Evap. at 140° F.	8.5	10.0 Max.
% Evap. at 158° F.	17.0	10.0 Min.
% Evap. at 221° F.	50.0	50.0 Min.
% Evap. at 329° F.	92.0	90.0 Min.
F.B.P.—° F.	361	....
Residue—%	0.9	2.0 Max.

TABLE 7—Properties of Finished Synthetic Diesel Fuel Supplied by Standard Oil Co. (N. J.) for the Navy Tests.

	Diesel Fuel to Navy	Navy Diesel Fuel Specifications Min.	Max.
Gravity, ° API	44.0	....	....
Color (R)	17½	4	....
Aniline Point, ° F.	176	....	....
Diesel Index	77.4	....	....
Sulfur %	Trace	....	1.00
Corrosion Cu Strip @ 212° F.	Pass	Pass	....
Cloud, ° F.	36	....	10
Pour, ° F.	30	....	0
Flash, ° F. (P.M.)	160	150	....
Vis. @ 100° F. SSU (K)	35.1	35	45
Carbon Conradson (10% Btms.)	0.009	....	0.20
Ash, Wt. %	0.0001	....	0.01
B S and W, %	Trace	....	Trace
Carbon, Wt. %	85.65	....	....
Hydrogen, Wt. %	14.35	....	....
Cetane No.	70	50	....
Distillation:			
Initial, ° F.	396	....	....
10% @ ° F.	439	....	....
50% @ ° F.	497	....	....
90% @ ° F.	620	....	675
Final, ° F.	678	....	....

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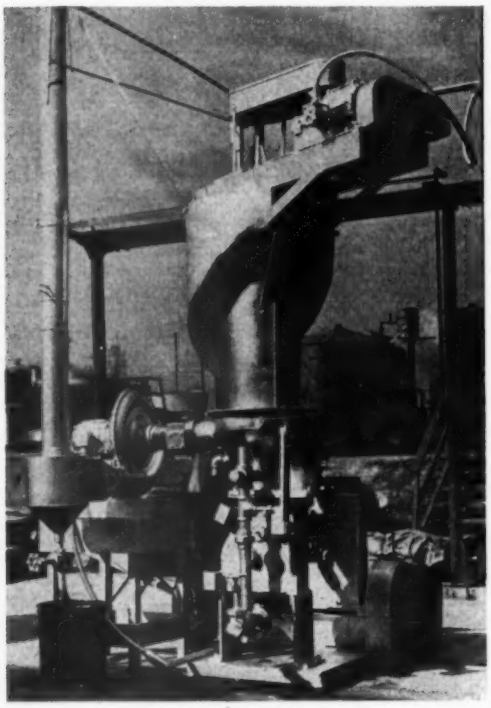


Fig. 3 (Left)—Shale kiln used in pilot plant work on synthetic gasoline and diesel fuels by Union Oil Co. of California. Union Oil is producing 1.8 b/d of synthetic oil based on Parachute Creek, Col., shale containing an average of one barrel of oil per ton

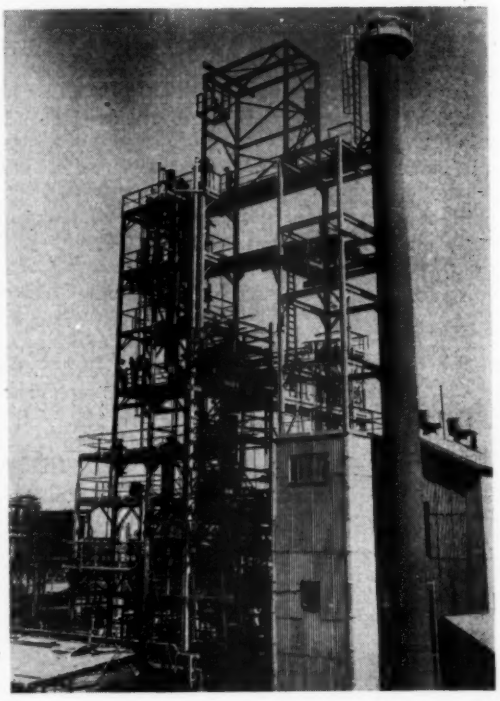


Fig. 4 (Right) — Standard Oil Co. of New Jersey produces synthetic oils from natural gas in this experimental plant at Baton Rouge. Approximately 10 b/d are manufactured using the "fluid" technique

or methods of manufacture of the compounds are not yet disclosed.

The Uncon LB series of synthetic lubricants are now being sold commercially in two limited areas as No. 300 "Prestone" motor oil, for use in cars, buses and trucks and tractors. These oils were introduced about a year ago for commercial use. They were used by the military services during the war and were the result of experimental work by Carbide and Carbon Chemicals going back for several years.

The LB-550, in the same series of synthetic lubes, is described as equivalent to most SAE 50 oils at 210 F. and lighter than most SAE 30 oils at 0 F.

According to Carbide and Carbon Chemicals, the LB synthetic oils may be prepared in any desired viscosity by controlling the reaction in the manufacturing process. It is not necessary to blend higher and lower viscosity oils, as is the general practice in preparing certain SAE grades from neutral and bright stocks, as is done with petroleum oils. The high viscosity indices characteristic of the lubricants, are inherent and not dependent on viscosity-index improvers.

The low API gravities of the Uncon oils coupled with high viscosity indices stamp them as being chemically different from petroleum oils. The synthetic lubes contain no wax or other additives to depress their pour point. The pour point is stable and can be reproduced after repeated temperature cycles. Flash and fire points compared favorably with mineral oils, although in the lower viscosity range, the flash points are said to be higher than for equivalent viscosity petroleum oils. The low carbon residue values shown by the synthetic lubes is believed indicative of low carbon formation.

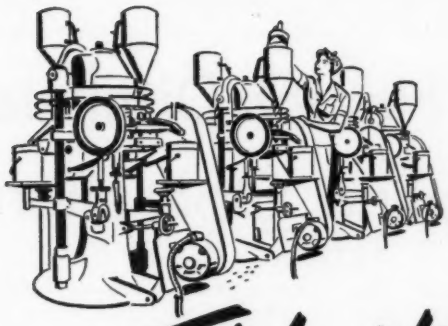
The oxidation products of the synthetic oils are for the most part low-molecular-weight volatile compounds, while in the normal process of oxidation of mineral oil, non-volatile products are formed which eventually convert to oil-insoluble sludges, gum and varnish. In the case of the synthetic lubricant, insoluble oxidation products which tend to foul an engine are not formed and this factor is said to be responsible for negligible increase in the viscosity of the lubricant with use.

In addition to the LB (water insoluble) series of the Carbide and Carbon synthetic lubricants, an HB (water soluble) series is also manufactured. These oils are being used commercially now in hydraulic fluids, as high-temperature, heat-transfer media, textile lubricants, in cutting oils, for wire and metal drawing operations, among other uses. Table 8 gives the properties of the LB-300 oil of the Carbide and Carbon Chemicals Corp. used in the Navy tests, and properties of the LB-550 aircraft oil.

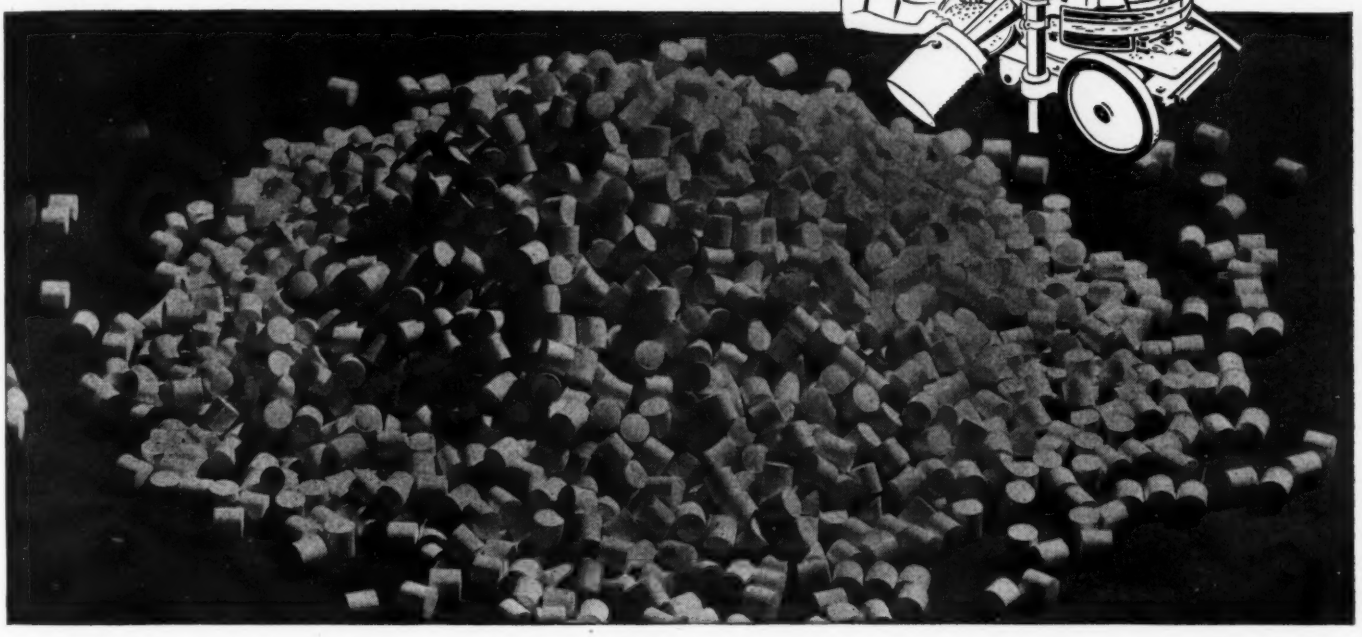
TABLE 8—Properties of Carbide & Carbon Chemicals Corp.'s LB-300 and LB-550 Synthetic Lubricating Oils Supplied for the Navy Tests.

	LB-300	LB-550
Viscosity, Say. sec. at		
210°F.	62.7	91.9
100°F.	300	550
0°F.	18,380	40,800
—30°F.	183,000	444,000
—50°F.	1,370,000	3,890,000
Viscosity, Centistokes at		
210°F.	11.0	18.5
100°F.	65.0	119
0°F.	4000	8900
—30°F.	40,000	97,000
—50°F.	300,000	850,000
V. I. (ASTM D-587-41)	142	140
Pour Point (ASTM D-97-39), °F.	—40	—30
Density at 210°F. (g/cc.)	.933	.939
Density at 100°F. (g/cc.)	.979	.985
Specific gravity at 60°F.	.997	1.003
Gravity API at 60°F.	10.5	9.5
Flash Point (ASTM D-92-33), °F.	470	510
Fire Point (ASTM D-92-33), °F.	570	580
Carbon Residue (ASTM D-189-41)	*	*
Ash (ASTM D-482-43-T)	*	*

*Less than .01 per cent.



Tabletted Catalysts



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Fluid Cracker Charges Heavy Distillate In Postwar Motor Gasoline Operation

THE Fluid catalytic cracking unit at the Avon, Cal., refinery of Tide Water Associated Oil Co. since the war has been operating on a charge stock of heavy California waxy distillate of high viscosity averaging 22-23° API gravity. During the war the unit was operated largely on straight-run gas oil of 30° or higher API gravity. At times also, various naphthas, both straight-run and cracked, were charged as supplementary feed to maximize aviation gasoline production.

The transfer to a heavier charge stock to produce motor gasoline was made gradually and without interrupting a run of 415½ days between turnarounds for the unit. This is said to constitute a record length of run for this type of refining facility. The unit started this run in July, 1945, and was shut down for a scheduled inspection and repairs on Sept. 8, 1946.

The heavy material for the present charge stock is obtained by deep vacuum flashing of heavy residuums from the crude stills in a vacuum feed preparation unit, which was installed at the time the Fluid unit was constructed. Results of cracking this heavy waxy feed stock for the production of motor gasoline are given in Table 1. These results are for operations on a catalyst comprised of a small amount of residual wartime synthetic catalyst to which a relatively large proportion of natural catalyst had been added.

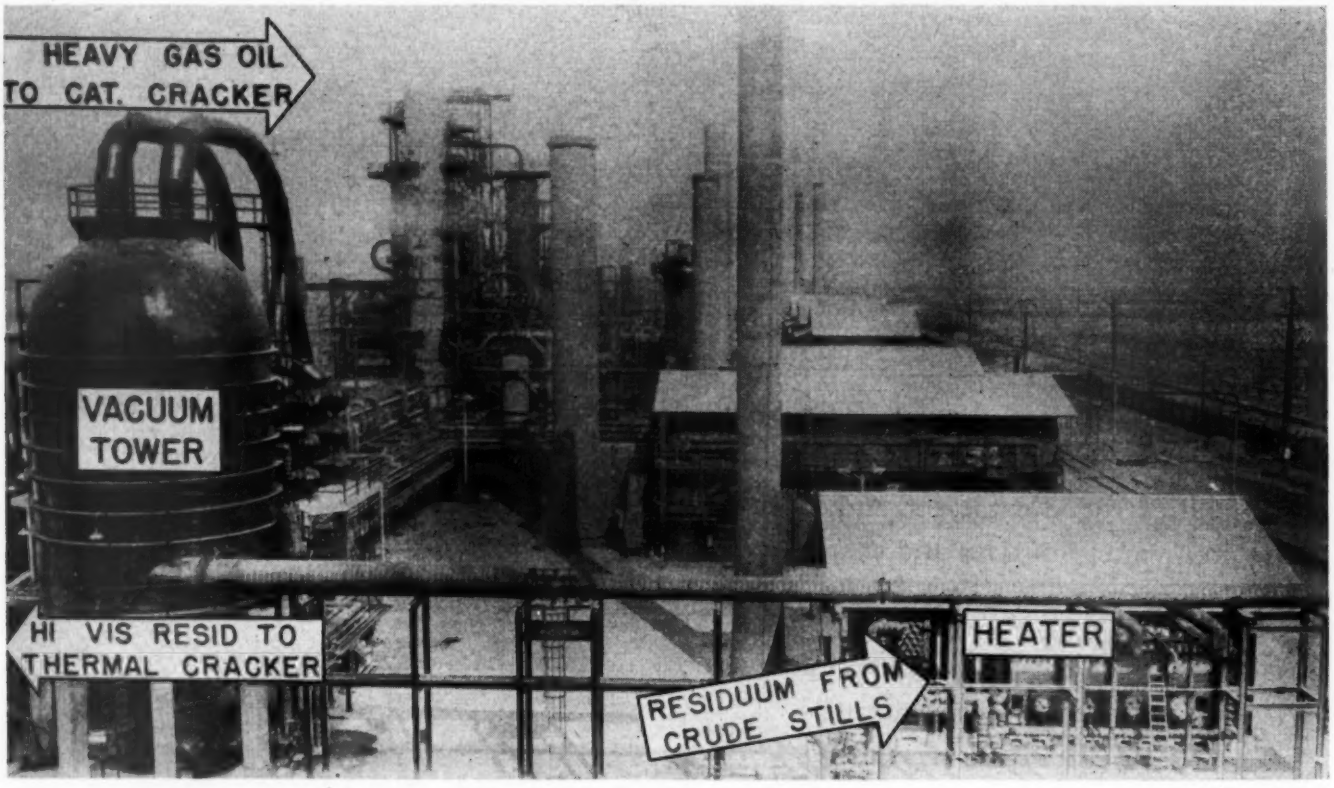
Typical analyses of the lighter hydrocarbon fractions from the present type of operations are given in Table 2, and Table 3 shows the operating conditions of the Fluid unit when making the products given in Table 1.

The record run of the unit at the Avon refinery was started on the aviation base stock type of operation using synthetic catalyst. With the end of the war operation was shifted to motor gasoline operation as fast as conditions would permit. As soon as stocks of synthetic catalyt on hand were used up, additions were natural catalyst. Since the commencement of postwar operations, natural catalyst costs have averaged approximately 2c/bbl. of fresh feed charged. Catalyst activity has been maintained at relatively high levels.

The record run of the Avon unit was terminated by failure of baffles in the Cottrell precipitator which shorted out part of the electrical system and caused excessive catalyst losses during the last few days of operation. Preliminary inspection shortly after the shut-down Sept. 8 showed the unit was otherwise in good shape except for certain work which had been anticipated. It would have been possible to continue operations for many more months, it is believed, had the electrical equipment been fully operable.

During the turnaround, a portion of the multiclone units was to be replaced and tubesheets repaired as necessary. A branched-pipe air distributor was to be installed at the end of the main riser below the grid in the regenerator. This change is the result of theoretical analyses and studies made in a glass model, which indicate that beneficial results may be achieved on distribution within the regenerator.

An additional recycle catalyst cooler originally purchased for extra wartime capacity was to be installed during the turnaround. All ferrules protecting tubes in the waste heat boilers operating on



Feed preparation unit for Fluid cracker at the Avon, Cal., refinery of Tide Water Associated Oil Co. Left is 25,000 b/d charge capacity vacuum tower; overhead lines are for gas oil charge to the cracker. Right is the tubular heater which brings straight-run residuum from the crude stills to approximately 690° F., when it is transferred to the vacuum tower

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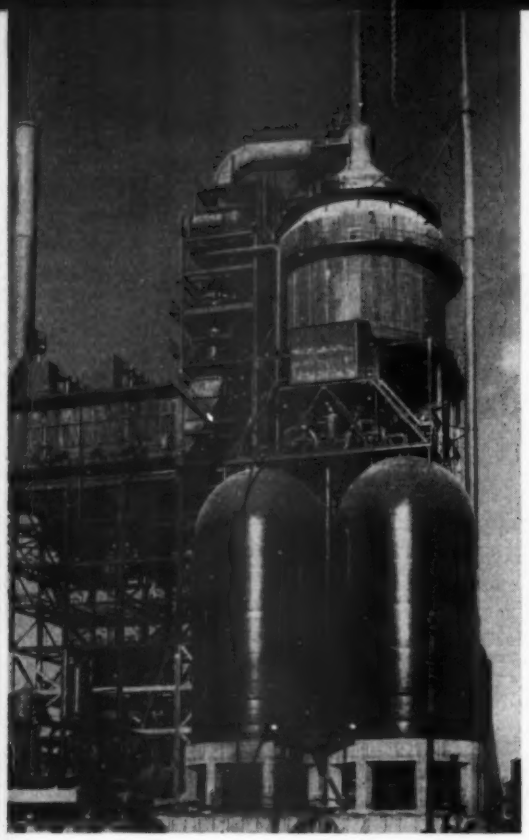


Fluid catalytic cracking unit at Avon refinery of Tide Water Associated Oil Co., which charges over 17,000 b/d fresh feed in motor gasoline operations. Spherical-topped vessels in foreground are for catalyst storage

flue gases were to be replaced. A new design of restriction grid was to be installed in the regenerator outlet to permit operating this vessel at a higher pressure. Some repair work also was to be done on the lining in the regenerated catalyst standpipe and in the flue gas line. The Cottrell precipitator was to be completely overhauled.

General process design of the unit, which was completed early in 1945, was by Universal Oil Products Co. in conjunction with Tide Water Associated engineers and those of the contractor, C. F. Braun & Co., which last named company contributed many design improvements. This unit is said to have the largest regenerator of any of the wartime Fluid units built. The regenerator is 46 ft. in effective diameter and 30 ft. high on the straight side between the top and bottom cones. Catalyst distribution is accomplished by a grid containing 2781 1½ and 2-in. holes representing about 3% of the grid area.

In the Avon installation no furnace is used to preheat the charge oil to the Fluid cracker. The oil charge, which is first preheated to about 400° F. through heat exchange, is contacted with the catalyst after regeneration at a temperature of about 1050° F. or higher for the latter.

The vacuum feed preparation unit at the Avon refinery is operated in conjunction with an existing thermal viscosity breaking unit. Straight-run residuum from the crude stills containing waxy gas oil is charged through heat exchange on the viscosity breaking unit into a 50,000,000 Btu per hour fired tubular heater designed to operate at transfer line temperatures up to 690° F. The transfer line enters the bottom section of a vacuum tower which is 24 ft. diameter and 22 ft. high on the straight side.

This vacuum tower is designed to operate at 50 mm. mercury absolute pressure in the flash section. It is provided with four specially designed fractionating trays and has a design charge capacity of 25,000 b/d of residuum, with the ability to take overhead 10,000 b/d or more of well fractionated oil. This product forms part of the charge to the catalytic cracking unit. The heavy residuum bottoms are thermally cracked in the adjacent viscosity breaking unit. The vacuum feed preparation unit was also engineered by C. F. Braun & Co.

Charges Heavy Distillate

TABLE 1—Results of Cracking 22-23° API Gravity California Waxy Distillate for Production of Motor Gasoline

(Yields and Product Inspections are Typical Monthly Averages)

Charge		
Fresh Feed, b/d	17,660	
Recycle, b/d	2,292	
Products—Basis Fresh Feed	**Vol. %**	**Wt. %**
Dry Gas	..	7.5
Propane-Propylene Recovered	3.8	..
Butanes-Butylenes	8.2	..
Light Catalytic Naphtha	18.1	..
Heavy Catalytic Naphtha	17.1	..
Light Catalytic Gas Oil	20.9	..
Heavy Catalytic Gas Oil	26.9	..
Coke	..	7.9

Product Inspection Data	**Feed Stock**	**Light Naphtha**	**Heavy Naphtha**
Gravity—°API	22.9	67.2	39.4
Viscosity SSU @ 100°F.	191	...	...
IBP—°F.	480	108	267
10%	659	129	285
50%	795	161	325
90%	934	218	392
Sulfur—Wt. %	0.4	0.1	0.2
Aniline Point—°F.	165	71	40
Carbon Residue	0.2	...	...
Octane—CFR MM—Clear	...	79	79
Octane—CFR RM—Clear	...	94	93

TABLE 2—Typical Analysis of Light Hydrocarbon Streams from Operating Fluid Unit on Heavy California Distillate

	Residue Gas	**Propane-Propylene**	**Butanes-Butylenes**
Hydrogen	30.6	..	..
Nitrogen	9.0	..	..
Oxygen	Tr.	..	..
Carbon Dioxide and Hydrogen Sulfide	2.2	..	..
Methane	28.2	..	..
Ethylene	6.7	0.4	..
Ethane	15.3	4.4	..
Propylene	4.6	63.4	..
Propane	1.8	31.8	..
Iso-butane	1 6	..	19.5
Butylenes	..	..	69.5
Normal Butane	..	..	11.0

TABLE 3—Typical Operating Conditions When Charging Heavy California Distillate to Fluid Cracking Unit

Oil Feed Temperature—°F.	500
Reactor Temperature—°F.	949
Regenerator Temperature—°F.	1105
Weight Hourly Space Velocity	6.3
Catalyst—Oil Ratio	10.3
Reactor Pressure—psig	9.1
Regenerator Pressure—psig	1.0
Reactor holdup—tons catalyst	22
Regenerator holdup—tons catalyst	323
Total Catalyst in unit—tons	760
Air Rate—MSCF per minute	51
Flue gas analysis:	
% CO_2	12.7
% CO	5.4
% O_2	1.7
Catalyst activity:	
Specific Surface sq.m./g.	100
Carbon on Regenerated Catalyst—Wt. %	0.17

Mechanized Accounting Streamlines Pipe Line Concern's Paper Work

New bookkeeping system built around a typewriting-computing machine provided a faster and more accurate means for handling the large number of small individual transactions with lease and royalty owners. Now one check covers all the interests of one individual. Records of leases and oil purchases are more accurately maintained. Space required for records is greatly reduced.

The accompanying article is based on material supplied by the Burroughs Adding Machine Co., Detroit, and the Bay Pipe Line Corp., Saginaw, Mich.

FASTER and more accurate accounting procedure was achieved by the Bay Pipe Line Corp., Saginaw, Mich., by swinging to mostly mechanized methods.

This pipe line system handles some 200,000 bbls. of crude per month. Its basic accounting objectives are: maintaining records of leases and of oil purchased; providing lease and royalty owners with statements of, and checks for, oil run from their holdings.

Before the change, the company had been going along with a system of largely handwritten records. Executives in the accounting department found this system produced unavoidable handicaps, among them:

Disadvantages of Old Methods

1. Errors inevitable in any system were discovered not currently but at month-end, during summarization and consolidation of daily figures. To trace them down meant wading back through a barrage of figures and records. Result was time wasted at a stage when time was at a premium.

2. Figuring was complicated, and involved many separate steps before the desired results appeared. As just one example, four separate operations were needed to determine taxes on crude oil run. First, the number of barrels was multiplied by the tax rate. Second, the value of those barrels was multiplied by the tax rate. Third, the two taxes were added together. Fourth, total taxes were subtracted from gross value to arrive at net value.

3. An excessive number of lease and royalty owner checks was written. Separate checks had to be prepared for each of an owner's interests, when the more desirable and efficient way would have been to issue each individual just one check covering all of his interests. Unfortunately, the system provided no practical means of centralizing all the activity information on the various interests for quick reference at check-writing time.

4. The system's records bulked so large that the office was cluttered with stacks of books, many containing information needed in day-to-day work. Aside from the inconvenience and disordered appearance, this presented the problem of not knowing exactly where to look for desired data.

5. Frequent overtime work and a never-ending "scramble" were necessary to get the work done, creating conditions unfavorable to efficiency and general peace of mind.

A look at today's procedure reveals how neatly Bay Pipe Line obtains, records and utilizes the figure-facts about its operations. The required computations are made in one fast, continuing operation.

How the New System Works

Field gaugers set the accounting cycle in motion when they prepare field tickets showing the number of barrels of crude oil placed in the storage tanks, the temperatures of the oil, its specific gravity, and other related information. The gaugers mail these tickets in to the Saginaw office each day and also telephone the information in daily.

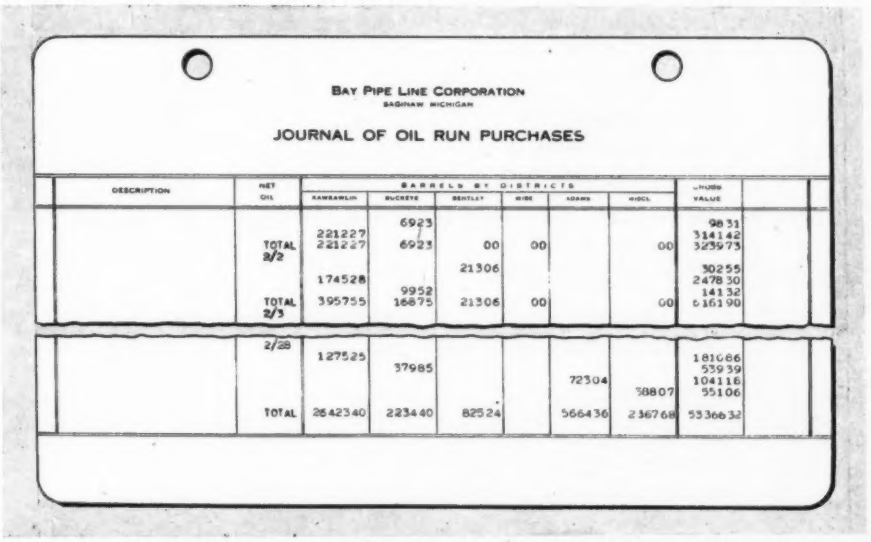
Using the phoned-in data as a base, the Saginaw accounting clerk adjusts the number of barrels by means of the Standard API gravity temperature correction tables, and prepares a complete summary, by fields, of oil purchased and handled that day, to-date, and in average for the month. She re-calculates this data from the tickets when they arrive and cross-checks the results with the summary figures already established.

Two or three times a month (exact frequency depends upon volume of purchases), field tickets for the period are posted to the Journal of Oil Run Purchased (Fig. 1). Total barrels for each field are multiplied by that field's posted rate to provide a gross value by fields. To-date totals of barrels for each field and of barrels and gross value for all fields are automatically accumulated by the typewriting-computing machine used on the work. These totals must balance with those previously established and proved in the summary report.

In this quickly-handled operation, Bay Pipe Line creates an accurate and complete record of purchases and, at the same time, sets up control totals to which subsequent record-posting will have to balance. The work is proved and balanced as it is done—an advantage that runs throughout the present system. Errors that may occur in month-end summarizing are localized to that summarizing operation making it unnecessary to pore back over the entire month's work.

System Also Saves Space

Today's records are more compact. For example, an entire month's activity can usually be posted on three Journal of Oil Run Purchases forms, measuring 11 and



BAY PIPE LINE CORPORATION
SAGINAW, MICHIGAN

JOURNAL OF OIL RUN PURCHASES

DESCRIPTION	NET OIL	BARRELS BY DISTRICTS						GROSS VALUE
		KAWKAWLIN	BUCKEYE	BENTLEY	MIDE	ADAMS	MIDCL	
		221227	6923					9831
	TOTAL 2/2	221227	6923	00	00		00	3141 42 3239 73
		174528		21306				30255 2478 30
	TOTAL 2/3	395755	9952 16875	21306	00		00	14132 5161 90
	2/28	127525	37985			72304	58807	1810 66 539 39 1041 16 551 06
	TOTAL	2842340	223440	82524		566436	236768	53366 32

Fig. 1—Form for Journal of Oil Run Purchases, and example of posting, as used by Bay Pipe Line Corp. in modernized accounting system

3/4 in. by 17 in. each. Bay accounting executives estimate that the space occupied by all records is somewhere between one half and two-thirds less than that formerly needed.

Following the Journal postings, the field tickets are sorted down by lease, and by date under each lease, so that the oil run information for the 10 or 15-day period can be entered on the Lease Statements. Value and barrel totals for all leases, automatically accumulated by the machine in this operation, must balance with the previous Journal posting control totals. Under the old system, there was no accurate means of reconciling these two posting runs.

Journal and Lease Statement entries are usually posted and balanced in two days or less. This despite the fact that ordinarily all lease accounts will be active in a 15-day period.

Taxes, Subsidies Computed Next

After group postings of daily detail on barrels and value have been completed for the month, taxes and subsidies, if any, are computed and printed at the top of each Lease Statement form (Fig. 2-A). To do this, the operator enters in the machine the number of barrels (1175.-29 in this case) and their value ($1668.-91) for the month. The machine multiplies them mechanically by the respective tax rates (1/8 cents and 2%). The total amount of tax ($34.85) is subtracted from the gross and the resulting net figure ($1634.06) printed on the form.

To pro-rate the total net value among the various interests comprising the lease is a simple, largely-automatic job. The machine operator enters the total value in the machine, then multiplies it by the decimals appearing at the left of each interest owner's name, which represent the fractional amounts of the lease that each owns. The machine provides an automatic total of the amount pro-rated; it must agree with the net total determined at the outset.

As a by-product of the pro-rating operation, the various net amounts are also printed on the individual interest statements of oil run, according to the pre-addressed, individual interest names (Fig. 2-B).

The data appearing in the top section of the Lease Statements is run off on the individual interest statements (varying in number from two to 75 for each lease) by means of a duplicating process.

Working and royalty interests are paid on the tenth of each month. The operator writes the checks on the typewriting-computing machine, obtaining the information from the individual interest statements. The suspense ledger provides the only other source of information for writing checks. It contains accounts that previously amounted to less than a dollar, that had no mailing address, or that were not paid because of some ownership litigation.

Check Writing Cut 50%

The concentration of complete activity information on each interest to either the individual tickets or the suspense ledger makes it possible for the girl to assemble the information quickly and to pay each owner with a single check no matter how many separate interests he may have. This feature cut Bay's check-writing volume in half, even though the number of interests to be paid has actually increased.

On the stub of the check (Fig. 2-C) is printed a detailed statement of the different leases from which the interests are being paid, the amount of each, and the total of all. Again, totals are balanced with the previously established control figures.

Carbons of the check and stub, made as a by-product of writing the checks, serve a dual purpose: (1) they are used to reconcile bank statements and (2) they form the basis, at the end of the year, for computing Bay's Form 1099 income tax purposes. Having, at most, only 12 checks for each interest for the year simplifies this job considerably.

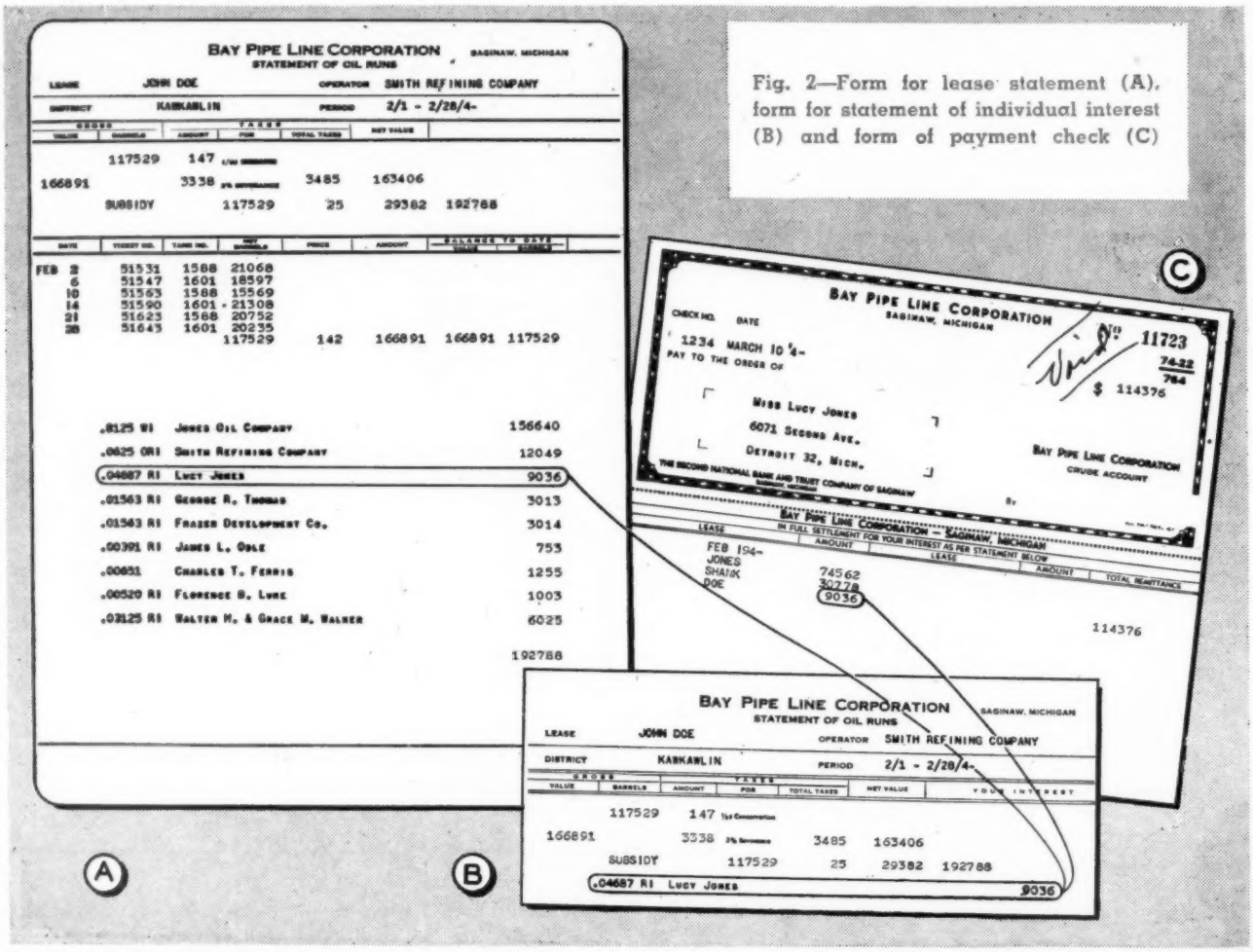


Fig. 2—Form for lease statement (A), form for statement of individual interest (B) and form of payment check (C)

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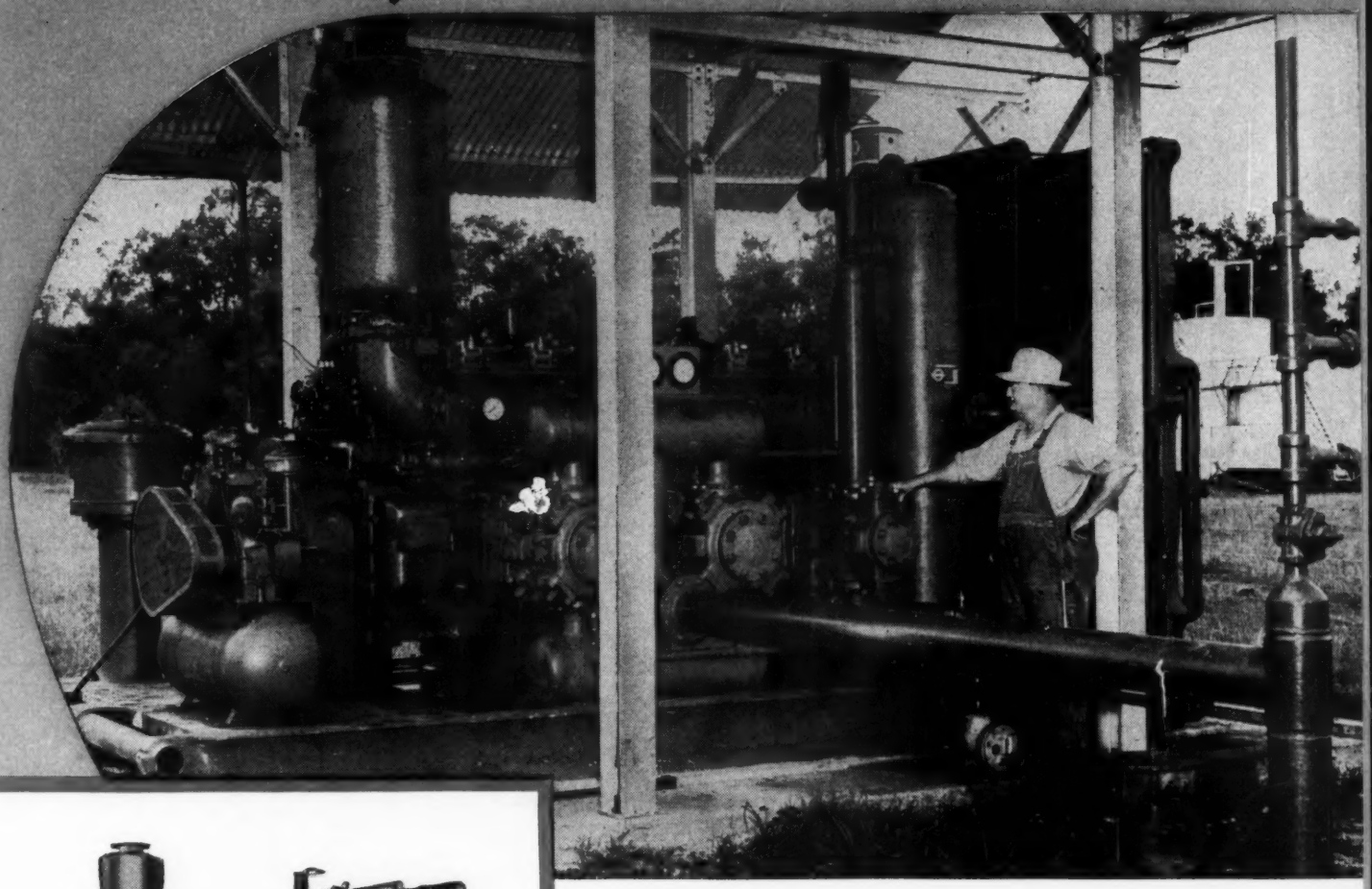

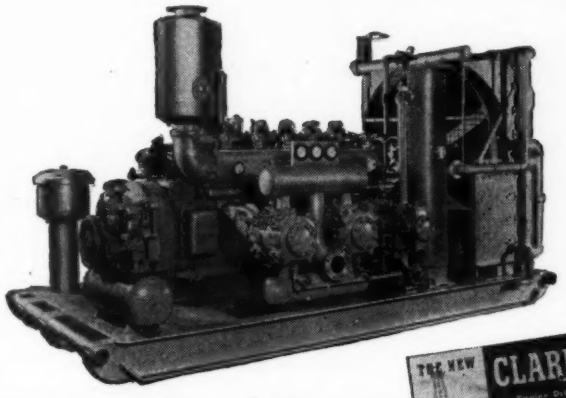

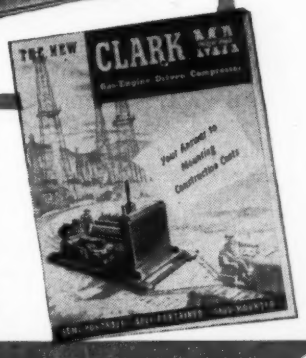

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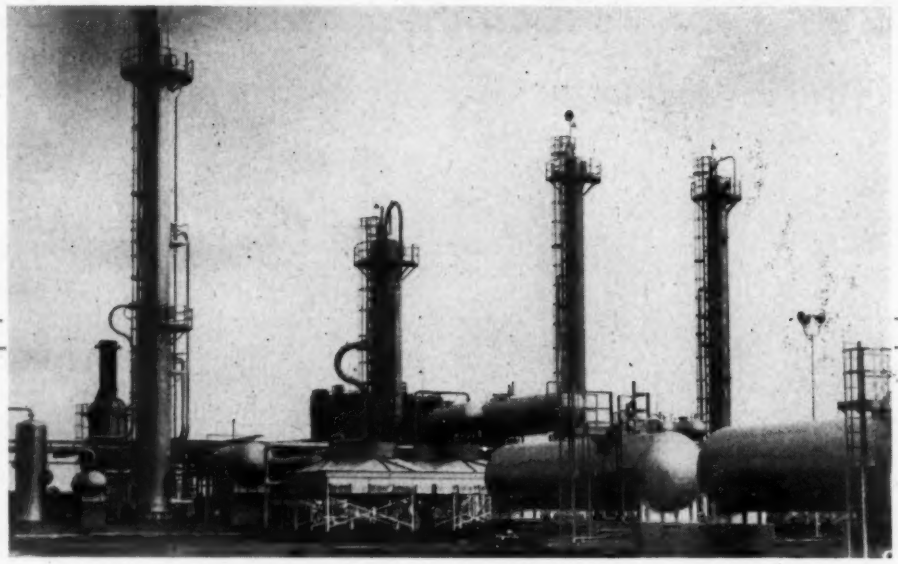

General view of process area at Warren Petroleum Corp. natural gasoline plant. Left to right: second stage scrubber, rich oil heater, absorber-deethanizer column, debutanizer, cooling tower (background), air-coolers (foreground), debutanizer, and depropanizer. Horizontal vessels at right are accumulators

Water Scarce—Natural Gasoline Plant Uses Air for 80% of Required Cooling

Engineering Innovations in Warren Petroleum Corp.'s $1,500,000 "Desert Type" Plant near Holliday Include Elimination of Steam, Use of Direct-Fired Oil Heaters

By D. P. THORNTON, Jr.
Assistant Editor
PETROLEUM PROCESSING

THE prototype of what may be the "desert-type" natural gasoline plant of the future, in that it uses no steam and only very little water, has been recently placed in operation by Warren Petroleum Corp., near Holliday, Texas.

It is a $1,500,000 project, combining natural gasoline extraction with repressuring facilities for the Hull-Silk, Daume and East Holliday Pools of Archer County, Texas. It handles 16,000,000 cu. ft. of gas per day and recovers 5 gal. of liquid products per 1000 cu. ft. of green gas processed. The chief innovations at this plant include:

1. **Elimination of steam generation by supplying heat required for processing from a direct-fired tube still in the distillation unit, which uses natural gas for fuel.**

2. **Utilization of air for at least 80% of the required cooling.**

3. **Operation of fractionator column reboilers with heat from the hot lean oil.**

4. **Utilization of hot lean oil for all other heating requirements, including plant buildings.**

The prime reason for these innovations was the lack of suitable water in sufficient supply for a plant of this size. What little water there is in the vicinity comes from wells and is extremely "hard". It would have been necessary to lay a pipeline from the plant site to Lake Kemp, 17 miles distant, and also build a pump station at the lake, to supply water for a conventional design of plant. In addition, an elaborate and expensive water treating system would have been required.

It was this situation, company engineers say, that caused several major oil companies to abandon plans for building a natural gasoline and repressuring plant in the area, despite the pleas of operators in the Archer county fields. In fact, several engineering contractors declined Warren's invitations to bid on the project because they did not believe the proposed unconventional construction would permit an economically feasible plant.

The fact the Holliday plant as built has met design estimates is a tribute to Warren's engineering organization and to J. F. Pritchard Co., Kansas City, the contractors, who together worked out the final design.

Surprisingly enough, despite its new features the plant cost but little more than had it been of conventional design, company officials say, because unusually large facilities would have been necessary to provide usable water. As it is, the water treating facilities are small. A single two-cell induced draft cooling tower with cooling sections installed below the V-pan is sufficient, and steam generating equipment and associated facilities have been entirely avoided.

The Holliday plant has been in operation approximately six months. Some minor difficulties in operation were encountered and corrected during starting up, but now the plant is operating well. Experience so far indicates the plant is simpler to operate than one of conventional design and requires less manpower. Company officials also believe maintenance will be considerably less, due to elimination of boiler-upkeep ex-

Keynote:

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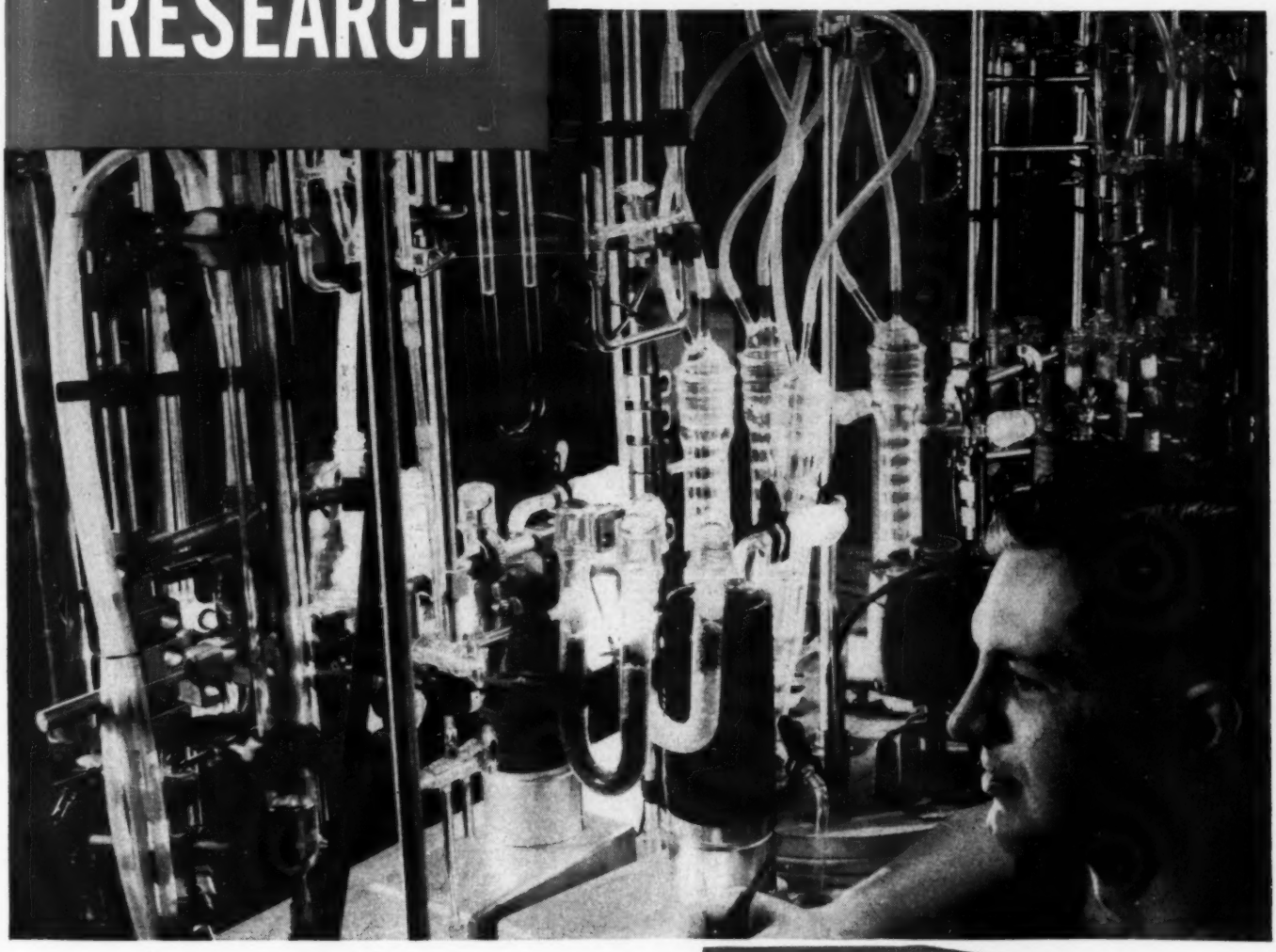
CONTINUING RESEARCH in the Du Pont Petroleum Chemicals Laboratory means improvement of additives now in use . . . development of even better petroleum chemicals for the future. It's your assurance of more and more service . . . more and more value for the products you sell. E. I. du Pont de Nemours & Co. (Inc.), Petroleum Chemicals Div., Wilmington 98, Del.



- GASOLINE STABILIZERS
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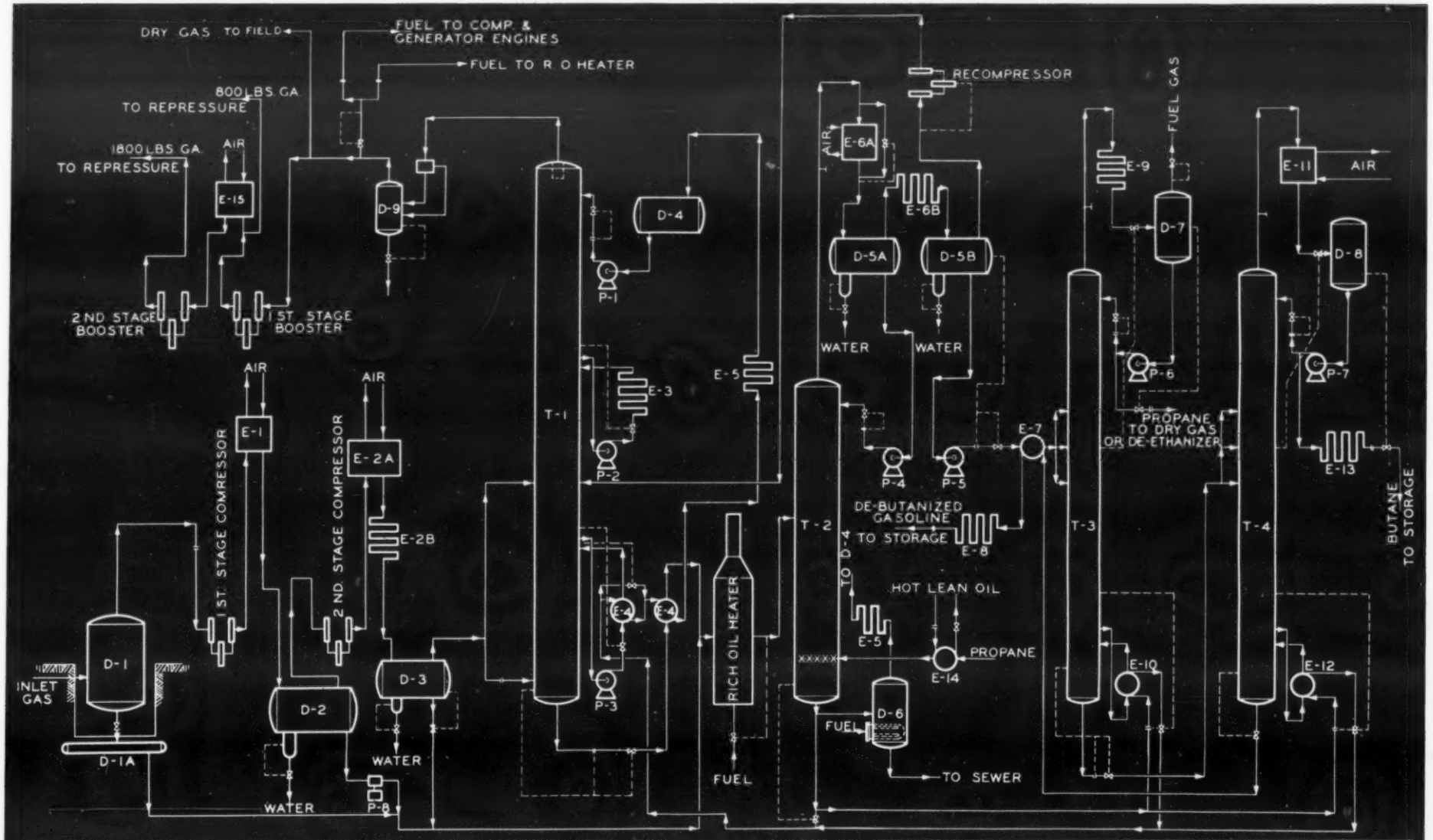
BETTER THINGS FOR BETTER LIVING . . . THROUGH CHEMISTRY



LEGEND

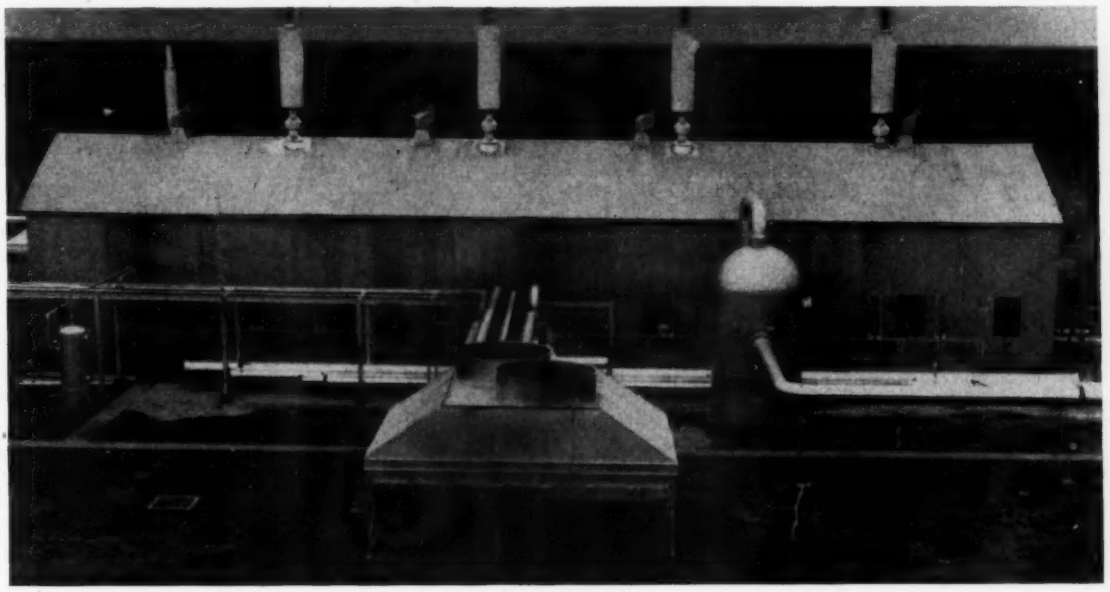
D-1 = INLET SCRUBBER.
D-1A = BLOWCASE.
D-2 = 1 ST. STAGE SCRUBBER.
D-3 = 2 ND. STAGE SCRUBBER.
D-4 = LEAN OIL SURAGE DRUM.
D-5A = STILL REFLUX TANK.
D-5B = MAKE TANK.
D-6 = LEAN OIL PURIFIER.
D-7 = DE-PROPANIZER REFLUX DRUM.
D-8 = DE-BUTANIZER REFLUX DRUM.
D-9 = RESIDUE GAS SCRUBBER.

E-1 = 1 ST. STAGE GAS COOLER.
E-2A = 2 ND. STAGE GAS COOLER.
E-2B = FINAL 2 ND. STAGE GAS COOLER.
E-3 = ABSORBER TOWER INTERCOOLER.
E-4 = RICH-LEAN OIL EXCHANGER.
E-5 = LEAN OIL COOLER.
E-6A = STILL OVERHEAD CONDENSER.
E-6B = STILL OVERHEAD FINAL CONDENSER.
E-7 = DE-PROPANIZER FEED PREHEATER.
E-8 = DE-BUTANIZER GASOLINE COOLER.

E-9 = DE-PROPANIZER OVERHEAD CONDENSER.
E-10 = DE-PROPANIZER REBOILER.
E-11 = DE-BUTANIZER OVERHEAD CONDENSER.
E-12 = DE-BUTANIZER REBOILER.
E-13 = BUTANE COOLER.
E-14 = STRIPPING PROPANE HEATED.
E-15 = 1 ST. STAGE BOOSTER GAS COOLER.

P-1 = LEAN OIL PUMPS.
P-2 = RICH OIL INTERCOOLER PUMP.
P-3 = RICH OIL CIRCULATING PUMPS.
P-4 = STILL REFLUX PUMP.
P-5 = DE-PROPANIZER CHARGE PUMPS.
P-6 = DE-PROPANIZER REFLUX PUMPS.
P-7 = DE-BUTANIZER REFLUX PUMPS.
P-8 = CONDENSATE PUMP.

T-1 = ABSORBER-DE-ETHANIZER.
T-2 = LEAN OIL STILL.
T-3 = DEPROPANIZER.
T-4 = DEBUTANIZER.



Main compressor building at Holliday. First and second stage fin-type coolers are at center in front of building. Vessel at right and behind cooler is inlet scrubber

pense. The tubular oil heater, which supplies all plant heat, should require but little repair attention.

As finally planned, the plant was to gather and process all casinghead gas from the three pools. The laying of more than 100 miles of pipeline was required, ranging in size from 24-in. down to 2-in., picking up gas at about 11.9 psia at plant inlet and compressing it to 200 psig plant absorption pressure. After processing, 6,000,000 cu. ft. of residue gas was to be compressed to 800 psig and 2,000,000 cu. ft. to 1800 psig and returned to the producing formations in the same ratio as received.

The plant itself was designed to extract a minimum of 60% propane and substantially 100% butanes, or 40,000 gal. of 26-lb. natural gasoline and 24,000 gal. butane-propane mixture daily. Provision also was included to increase propane extraction whenever desired by increasing the oil rate to the absorber. Analysis of the inlet gas is given in Table 1.

Hot Lean Oil Supplies Process Heat

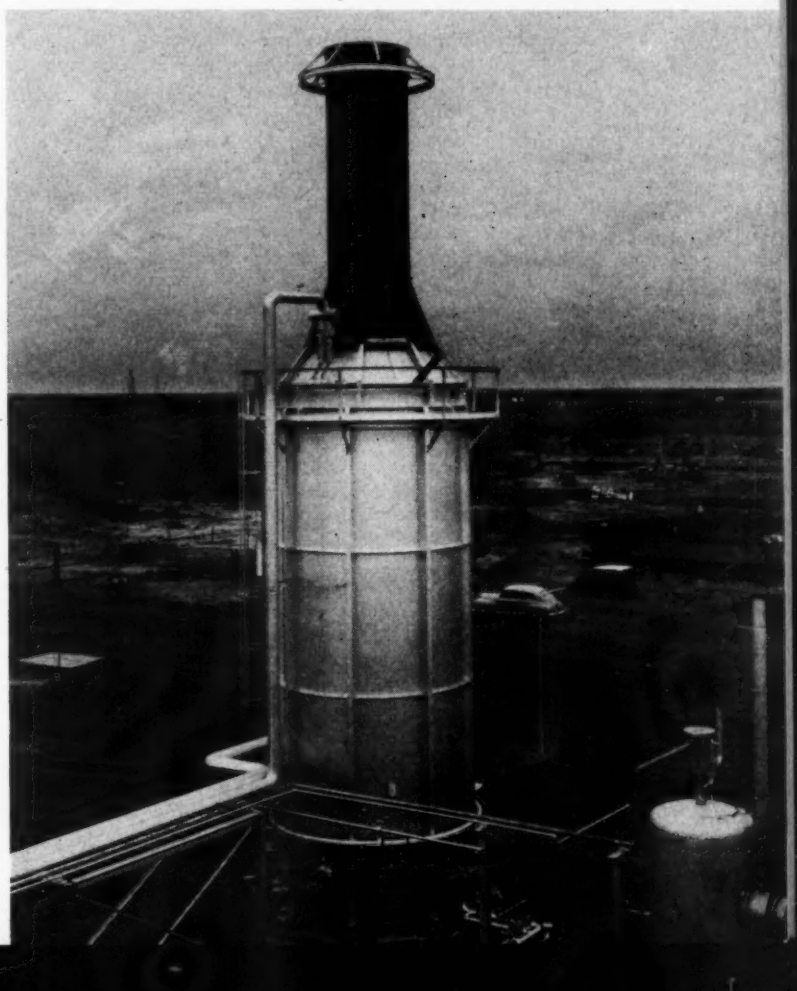
All process heat was to be supplied by hot lean oil from the still, necessitating somewhat more oil than would otherwise be required and adding to the normal duty for hot oil pumps and rich oil heater. Depropanizer overhead condensate was selected as the still stripping medium, to be flashed into the still following exchange with hot lean oil from the still bottoms.

Over 80% of the plant cooling load was to be handled by fin-type air coolers, the duty for which includes cooling engine jacket water, cooling on the first stage of gas compression, primary cooling on second-stage gas and primary cooling for still and debutanizer overheads.

Use of make up water was restricted to engine jackets and cooling tower. The products cooled by water are limited to final cooling on second stage gas (summer only), absorber intercooler, lean oil coolers, still overhead condenser (final cooling only), depropanizer overhead, debutanizer base and butane product cooler. A small continuous softener, utilizing soda ash, lime and alum, was in-

TABLE 1—Analysis of Raw Casinghead Gas Received at Holliday Plant

Component	Mol-%
Methane	65.64
Ethane	9.99
Propane	11.90
i-Butane	1.35
n-Butane	5.37
i-Pentane	1.89
n-Pentane	2.26
Hexanes-plus	1.60
	100.00



Warren's rich oil heater is of the vertical tubular type, direct fired with natural gas, which supplies all process and building heat for the plant in lieu of steam. To right of heater is specially designed purifier for absorber oil. Purifier is described on page 17 of this issue, under "Plant Practices"

Fig. 1—Conventional flow diagram of Warren Petroleum Corp. natural gasoline plant near Holliday, Texas

stalled to take care of the limited quantity of makeup water thus involved.

The "Alco" fin-type coolers, utilizing induced draft air as the cooling medium, are unique in natural gasoline plants. So far as is known, the Holliday plant is the first in the industry to use them to such an extent for general process cooling, although as the radiator on an automobile or internal combustion engine they are commonplace.

At Holliday these coolers consist of several open sections of finned tubes, mounted in a housing open at the bottom and closed by the fan-housing on top. The fan is shaft-driven by an electric motor mounted on the cooler foundation. This equipment was manufactured by American Locomotive Co., New York.

Advantages of Air Coolers

The advantages of the air-cooled heat exchangers are stated by the manufacturer to be: (1) Operation is not affected by wind velocity or direction as regards efficiency; the natural draft construction may reduce power requirements sufficiently to permit operation at times without use of the fans. (2) Cooling surfaces are so positioned as to minimize damage by wind-driven sand, rain and hail. (3) Separate surfaces for separate cooling duties can be mounted in the same unit. (4) Fans can be driven by any type of power desired. (5) Headers are designed to vary the numbers of passes to fit process requirements for a given job, allowing selection of minimum surface within pressure drop limitations of the process, maintaining maximum velocity required for highest heat transfer rate.

The air coolers employ fin tube surfaces of two types. Those for cooling engine jacket water use radiator sections consisting of several rows of tubes passing through thin plates and bonded to them. Air passing over the tubes and between the plates picks up heat. The radiators are suspended from the structural steel frame underneath the fan.

The gas cooling and condensing units employ tubular bundles of a design similar to those used for many years in atmospheric cooling towers. The fin tubes are rolled into the header boxes. Opposite each tube end is a plugged opening to permit rolling of the tube and also for cleaning, if necessary. The complete bundles are hung from the structural steel frame under the fan. All of the heat transfer surface is either Admiralty metal or copper.

Each Air Cooler Self Contained

Each air cooler is a self-contained unit, in that it includes the cooling fluid circulator. This circulator is a propeller type fan with the fan located above the cooling surface, thereby operating as an induced draft fan. With the induced draft fan, the air is drawn over the heat transfer surface at a relatively low velocity and discharged to the atmosphere at a much higher velocity.

TABLE 2—Analysis of Dry Gas from Holliday Plant

Component	Mol-%
Methane	83.05
Ethane	10.61
Propane	6.32
i-Butane	0.02
	100.00

All pumps in the plant are electric-driven horizontal centrifugals except the cooling water circulating pumps, which are vertical mounted, deep-well centrifugals, and the products pumps for shipment to the loading rack, which also are deep-well type centrifugals. The fire pump is driven by a gasoline engine.

Compressor horsepower totals approximately 5000, divided between that used in boosting intake gas to 200 psi absorber pressure and that for the repressuring project. All are gas-engine driven. Electric power is generated by three 370 h.p. gas engines driving 312 KVA generators and 7.5 KW belt-driven exciters; power is 440 v., three-phase, 60 cycle alternating current.

Water for engine-jacket makeup comes entirely from that condensed from the raw gas following the second stage of compression to plant absorber pressure, which amounts to about 1000 gals./day. The excess also supplies a portion of the cooling tower makeup; already soft, it requires no chemical treatment. Balance of plant water now comes from a small well near the property, which also will supply water for fire fighting. A line being laid from the nearby town of Holliday will augment this supply and also provide drinking water.

All control instruments are installed in a control room centrally located in the process area. Air for actuation is scrubbed and dehydrated to prevent fouling of lines and valves.

Process Description

Raw gas from the field at 11.9 psia pressure is first scrubbed to remove any entrained liquids and compressed through two stages to 200 psi. First stage cooling is accomplished with a finned-type cooler, as is primary cooling of second-stage discharge. Final second-stage cooling—in summer only—is attained by open sections in the cooling tower. The processing arrangement is shown in Fig. 1.

The green gas then passes to a 30-tray combination de-ethanizer and absorber. The top 20 trays of this tower operate conventionally as an absorber, equipped with a water-cooled intercooler on the 13th tray from the top. Rich oil from the absorber section bottom tray is circulated through a rich-to-lean oil exchanger to pick up heat and returned to the top of the 10-tray de-ethanizer section of the tower as reflux against a small stream of raw gas admitted at the bottom for agitation and to help sweep out ethane and lighter. Bottoms then are charged to the rich oil heater.

Dry gas, absorber overhead, passes through two mist extractors which recover a considerable amount of oil from the gas if the absorber is heavily loaded and thence to plant fuel, for fuel use in the field and to compressors for repressuring the oil pools. Table 2 shows the composition of this material.

Propane Used for Stripping

From the heater, rich oil passes to the still, which is conventional except for the fact that propane, heated to 400° F. by exchange with hot lean oil leaving the still, is used instead of stripping steam. It is introduced through a spider near the still bottom. Overhead is partially condensed in an air cooler, passes through the reflux accumulator and final condenser (open coil water-cooled) into the make-tank.

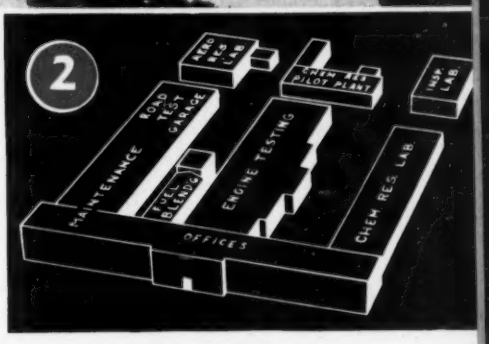
Hot lean oil from the still is made to pay its way. A sidestream from the still bottoms is utilized to heat a portion of the depropanizer overhead condensate used for agitation in the still, the balance of the lean oil providing reboiler heat to depropanizer and debutanizer side streams, plant buildings, and to heat fat oil at the combination de-ethanizer and absorber. Another small sidestream from still bottoms is passed through a lean oil purifier on its way to the lean oil surge tank. This purifier is direct-fired with gas, vaporizing the lean oil to remove heavy ends. (A detailed description of the lean-oil purifier appears in the "Plant Practices" section of this issue, pg. 17.)

Since it was not intended to split the butanes and pentanes, only two 30-tray fractionators were installed in the plant to produce propane-butane mixtures and natural gasoline. Provision has been made for the installation of additional fractionation facilities, if and when needed to make other products.

Still condensate is pumped from the make-tank to the depropanizer through an exchanger where heat is picked up from debutanized gasoline. In this conventional 30-tray column partial depropanization occurs, the bottoms product passing to a 30-tray debutanizer. Overhead is condensed through open sections in the cooling tower . . . used for reflux and as a stripping medium in the still. The excess is piped to dry gas disposal.

In the debutanizer, natural gasoline of any desired vapor pressure is withdrawn as bottoms, passing to storage through heat exchange with still-make and final cooling in open coils in the cooling tower. The overhead product, a propane-butane mixture, is condensed by fin-type air coolers and finally cooled by water-cooled open sections in the cooling tower.

Fuel Research by Mass Production Methods



SCIENTIFIC research by "mass production" methods has been developed to a high degree by the Ethyl Corp. at its Detroit Laboratories. Using many new techniques for multiple chemical analyses and over 50 engine test stands, that company has devised ways for carrying out simultaneous studies on a wide variety of fuel and engine problems.

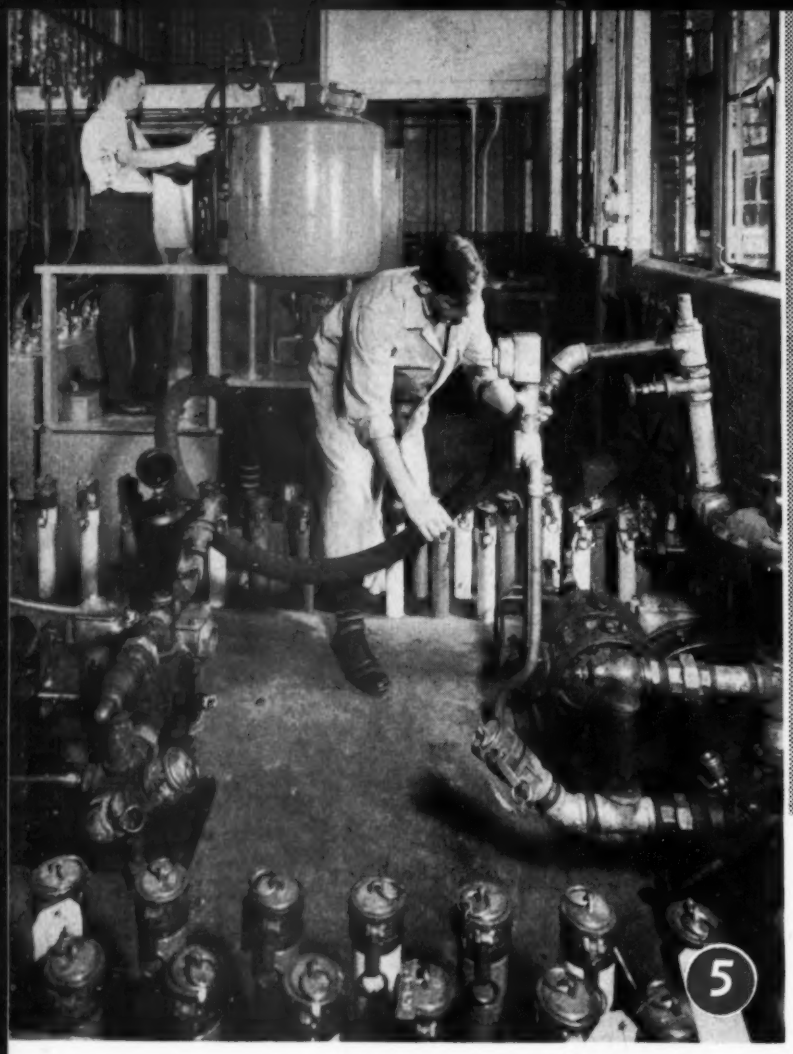
The methods and equipment Ethyl uses were revealed Nov. 14-15 when representatives of the petroleum, automotive and aircraft industries were invited to inspect the company's Detroit buildings, completed in December, 1941, but since closed to the public.

A major part of the more than 123,000 sq. ft. of floor space in the six main buildings, which include nearly 70 chemical and engineering laboratories, is devoted to fuel problems—ping, knock, TEL improvement, and the like.

The pictures on this and the next two pages illustrate in part what goes on in Ethyl's Detroit laboratories, shown in general aerial view 1 and sketch 2.

In the chemical pilot plant is a complete 1/100th scale TEL manufacturing plant in which extensive experimental work is done. A technologist is shown at 3 charging the alkylation autoclave, which is part of this unit.

The apparatus seen at 4 is used in the organic laboratories to determine the lead content of fuels before they are engine-tested. In addition to experimental blends made in its laboratory,

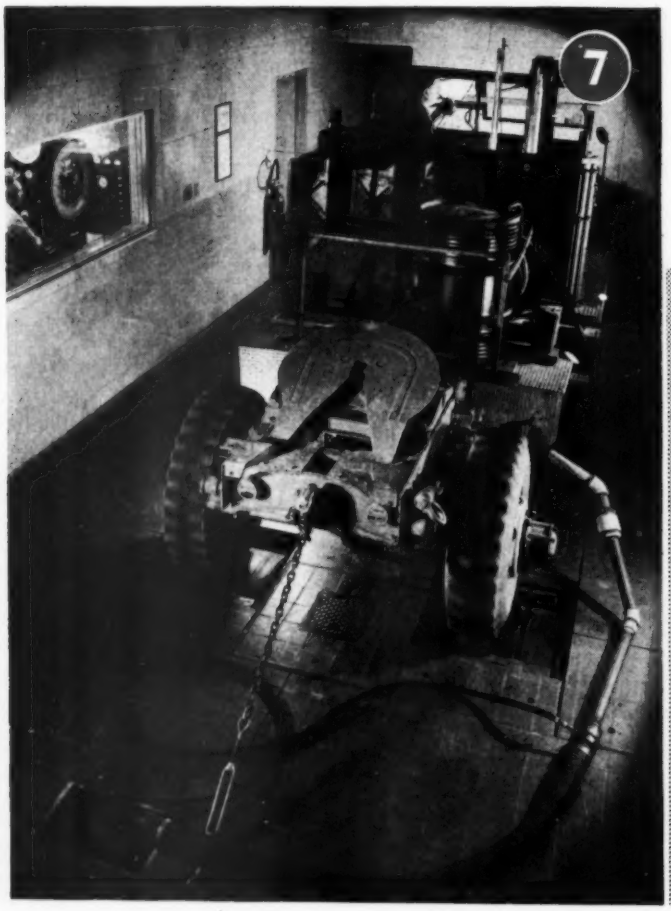


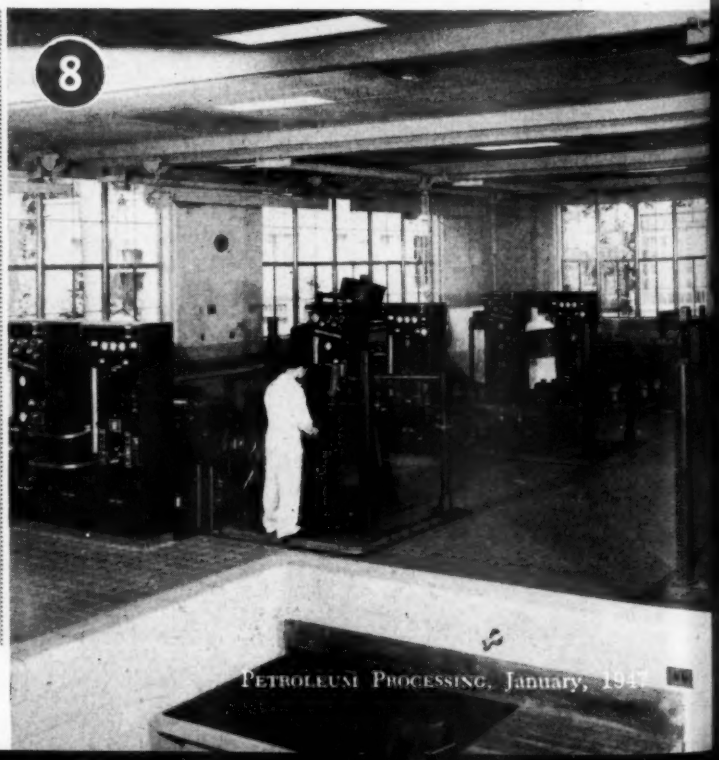
Ethyl checks products of the many oil companies with whom it works on mutual research problems.

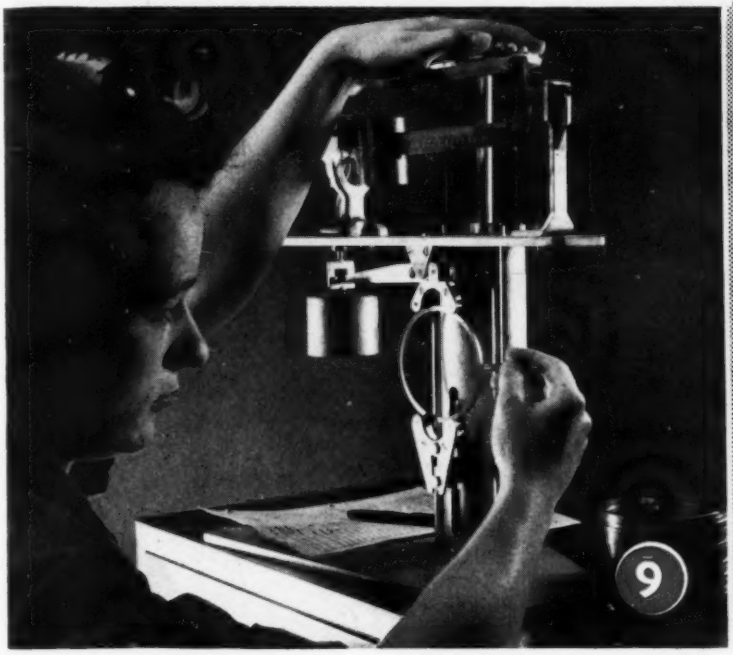
A total of 34 underground fuel storage tanks, ranging from 500 to 10,000 gallons capacity each, supply test fuels for the various engine laboratories. Equipment for blending these fuels in the desired proportions is shown at 5. Suction and fill pipes are arranged in two groups (foreground) with three transfer pumps between them. Pumps, pipe ends, and connecting hose are equipped with quick-coupling fixtures. A 90-gallon, agitated tank on platform scales in middle background provides additional blending facilities for small quantities of fuel.

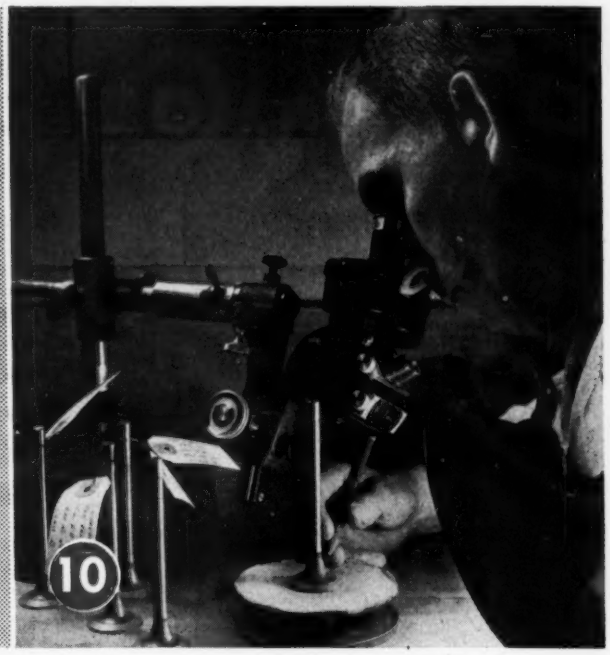
Distribution of either blends or straight fuels to the feed tanks at the various engine test stands is accomplished by means of a "fuel switchboard", 6. Quick-coupling fixtures are again used here. Pipe ends in the bottom panel lead to the engine stands; those in the upper panel lead from the gravity feed tanks to which fuels to be used are first pumped from storage or blend tanks.

For some engine tests Ethyl uses full-scale automotive equipment in rooms under carefully controlled conditions. A truck









tractor is under test in the "hot" room in 7. Rear drive wheels of truck revolve on drums flush with the floor, transmitting power against a dynamometer, by which means engine output is measured. Room temperature can be varied from 25 to 150° F. Blast of air at front of vehicle can be supplied at controlled velocities corresponding to apparent speed of truck at rear wheels. Engineer in control room, seen through window at left, is in telephonic communication with engineer in truck cab.

In a "cold" room, similar equipment enables Ethyl to check fuels in cars and trucks under temperature conditions as low as 50° below zero.

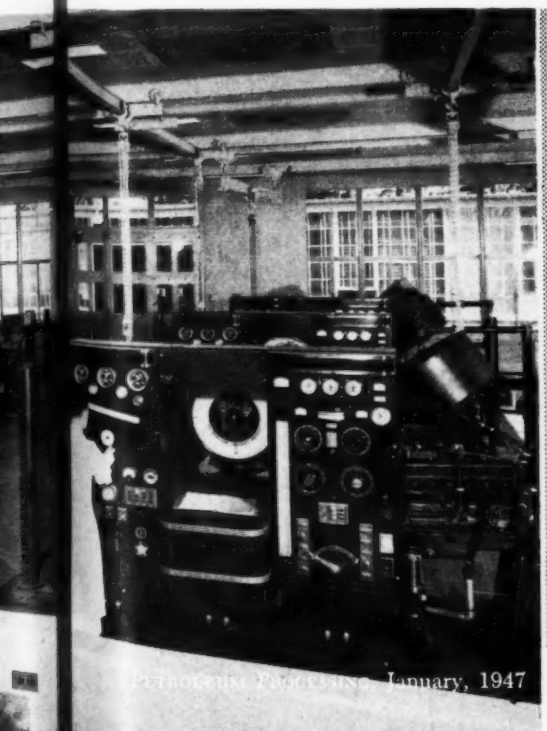
In addition to such special study rooms, equipment is provided for multi-cylinder engine durability tests in the 60 x 54 ft. room shown at 8 containing six double-end dynamometers. Each stand is self-contained with respect to control panel, fuel supply and the like. Overhead tram cranes handle engines and other accessories for servicing. Double-end dynamometers permit running one test engine while a second is being torn down or repaired.

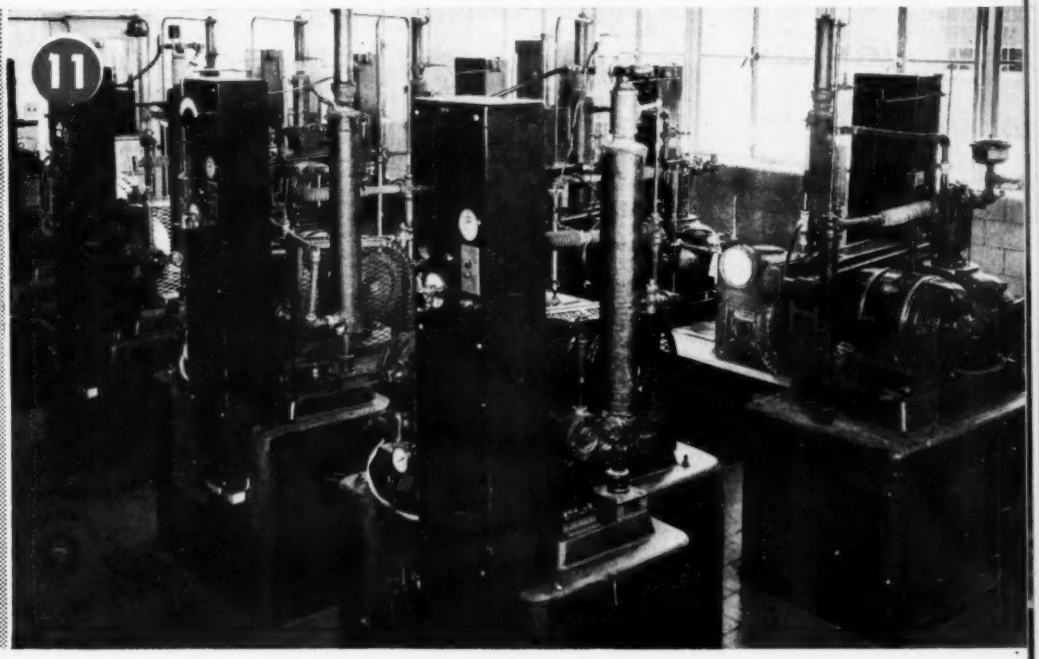
Single-cylinder engine durability tests are conducted on the set of 10 units shown in 9 in a room adjacent to that shown in 8. Equipment is the same type, but smaller in size than that shown in the larger room. Dynamometers are single-end style.

After test runs, engines are dismantled and examined. Each part undergoes rigid inspection to determine the effects of different fuels. Apparatus for measuring piston ring tension is shown at 10 and for microscopic study of an exhaust valve at 11.

Performance data on engines, engine parts, fuels, lubricants, and all accessories is then collected and studied in correlation to chemical and metallurgical analyses. The problem to be met in each case is different, depending upon where the improvement is desired.

Ethyl's original laboratories were moved from Yonkers, N. Y., to Detroit in 1927, and greatly expanded, especially in the line of aircraft fuel and engine research. The first site in uptown Detroit did not permit space for sufficient expansion, so the present location, a 26-acre tract in Ferndale, a Detroit suburb, was acquired and construction of the pilot plant begun in 1936. The Chemical Research group was moved to Ferndale in 1939, and the existing facilities finally reached completion in 1941.





Another BECKMAN pH Advancement!

THE BECKMAN MODEL H PORTABLE AC pH METER

Some Important Features of The Beckman Model H

Full AC Operation: The Model H is completely self-contained and operates directly from standard 115 volt AC lines without accessory equipment of any kind.

High Accuracy: The accuracy of the Model H instrument is equivalent to that of the well known Model M and Model G Beckman pH Meters. For rapid work, accuracies of 0.1 pH unit are easily obtained, and more careful attention to technique permits determinations to 0.02 pH units. Such high accuracy has never before been available in a compact AC pH Meter.

Single-Point Buffer Calibrations: With the Beckman Model H it is not necessary to calibrate with two buffer solutions. The Model H incorporates a unique electronic circuit that permits accurate readings regardless of variations in resistance of the glass electrodes due to aging or due to electrode temperature changes after calibrations. This important advantage is accomplished without need for multiple buffer calibrations.

Maximum Temperature Stability: After a short warm-up period, subsequent change in calibration of the instrument due to temperature effects is very small—only about 0.1 pH unit in the first two hours and 0.05 unit subsequently. When maximum accuracy is required, this change may be instantly checked and corrected *without rechecking against buffer solution.*

Full Temperature Compensation, 0 to 100° C: A built-in temperature compensator covering the full range of 0° to 100° C can be set to compensate automatically the effect of temperature changes on the EMF of the glass electrode over the entire pH range of the instrument. Thus, the pH at the electrode temperature may be read directly from the dial without calculation or corrections.

Direct Millivolt Scale: The Model H Meter is graduated in millivolts as well as pH units, and a range switch permits measuring directly either in millivolts or pH at will.

Rugged Lightweight Construction: The Model H is housed in a cast aluminum case with an attractive dark gray wrinkle finish. The instrument weighs approximately 10 pounds, complete, and is easily carried. For maximum operating convenience the meter dial and all controls are mounted on a sloping panel.

The First Portable AC pH Meter with DC Accuracy, Simplicity and Dependability

NO LONGER need you sacrifice accuracy and dependability to get the convenience of AC operation in a portable pH Meter. For now the same organization that pioneered modern glass electrode pH equipment, and has pioneered every major advancement in modern pH instrumentation and methods, brings another important development...a portable pH Meter that operates from standard AC current *without sacrificing any of the accuracy and dependability that are so essential in modern pH applications.*

This new instrument – the Beckman Model H pH Meter – has been in development over a long period of time. Many different designs and circuits were tested and rejected before an instrument was perfected that meets the rigid Beckman standards of excellence. The Model H Meter is not just an "AC" pH Meter. It is an instrument embodying advancements in circuit design that insure the same high operating efficiency and accuracy that have made Beckman pH Equipment standard throughout the world.

A few of the many unique features incorporated into the Beckman Model H pH Meter are outlined at right. Contact your nearest distributor of Beckman pH Instruments for further details...or write direct. *Beckman Instruments,* National Technical Laboratories, South Pasadena 23, Calif.

BECKMAN **INSTRUMENTS CONTROL MODERN INDUSTRIES**

AN

PAPER

Correlation of Operating Variables In the Naphtha Polyform Process

By JOEL H. HIRSCH, P. OSTERGAARD and W. C. OFFUTT

A procedure for calculating yields, octane numbers, and required operating conditions in the Naphtha Polyform Process is discussed and illustrated with examples. It involves use of the "C_2's and Lighter" formed as an appropriate index of the severity of treatment, a method which the authors predict may be a promising new instrument for other thermal conversion operations.

The Naphtha Polyform Process is a thermal method for upgrading naphthas and low-octane straight run gasolines. It was the subject of three papers presented at the recent API meeting in Chicago (Nov. 11-14). Two of the three papers were published in their entirety in the December issue of Petroleum Processing (pp. 267 and 278) and described the process, recent improvements in it, and the charging of excess refinery gases with the liquid stocks. This present paper is the third of the series.

Acknowledgement

Presented before Division of Refining, American Petroleum Institute, Chicago, Nov. 12, 1946.

Joel H. Hirsch and W. C. Offutt are with Gulf Research and Development Co., Pittsburgh, and P. Ostergaard with Gulf Oil Corp.

TO PROVIDE the most efficient utilization of the Polyform Process in present day refinery operations, a generalized correlation has been prepared, based on data from a large number of pilot plant runs. Using this correlation, it is possible to calculate the yields of hydrogen, methane, ethane, ethene, propane, propene, butanes, butenes, isopentane, n-pentane, pentenes, C_6 — 400° F. E. P. fraction, and tar; CFR motor and research octane numbers, clear and leaded; the rate at which propane, propene, butanes, and butenes must be recycled for a given conversion; and the amount of reaction coil volume required to obtain the desired conversion with a given heater temperature gradient.

While the correlation is general the examples in the present paper deal with the polyforming of 200-400° F. Eastern Venezuela naphtha (Table 1) at 1500 psi, both with and without the addition of outside C_3 fractions, and illustrate the calculation procedure employed. The complete correlation covers 139 pilot plant runs on 17 charge stocks, ranging from Rodessa naphtha, of 12.2 characterization factor [3] and 22 CFR M octane number, to catalytic cracked naphtha, of 11.1 characterization factor and 77.4 CFR M octane number. It is applicable both to straight or self contained polyforming and to polyforming with the addition of outside C_3 and C_4 fractions, ranging up to 60 vol. % of the naphtha charge and varying in olefin content from zero to 60 vol. %.

TABLE 1—Properties of Eastern Venezuela Naphtha Charge

Gravity, °API	46.8
ASTM Dist., °F.	
I.B.P.	220
10%	304
30%	318
50%	329
70%	342
90%	374
E.P.	420
Aniline Point, °F.	117
CFR M Octane Number	45.6
CFR R Octane Number	47.9
Characterization Factor[3]	11.67

In making this correlation the pilot plant data were first converted to a once-through basis from a series of material balances around the stabilizer and absorber. The amount of each component from hydrogen through tar entering and leaving the polyform coil was determined for each run. In this way the straight polyform runs and runs with outside gas were placed on a comparable basis, the principal difference being in the relative amounts of some components such as propane and propene present at the coil inlet. This difference made possible calculation of the effects of individual components on yields and octane numbers.

Experience in previous correlations has shown the convenience of using an appropriate severity index which can be related to product yields and product characteristics on the one hand and to operating variables such as time and temperature on the other. Having placed all of the polyform runs on a common basis, the next step was therefore to find a suitable severity index. Selection of a severity index for the Polyform Process was limited by the fact that so many of the light gaseous components are recycled. It was necessary to find an index in which no substantial amount of the components would be recycled, or if recycled would not be further converted to any appreciable extent. This narrowed the choice to "C_2's and Lighter" formed during operations, expressed as wt. % of the total stream fed to the reaction coil. Reaction velocity studies later showed that this was a fortunate choice.

It has been found that yields, throughputs and product characteristics can all be related as functions of four major variables:

1. Character of fresh charge, as defined by naphtha octane number and characterization factor and by amount and composition of outside gas.
2. Severity of treatment, as indicated by the "C_2's and Lighter" severity index.
3. Extent of recovery and recycling of C_3 and C_4 fractions as determined by operation of the absorber and stabilizer.
4. Operating pressure, which is a variable of lesser effect than the other three.

Yield Correlation

Preparation of the yield correlation was aided by the fact that a number of pilot plant runs were made charging practically pure propane as outside gas. From the increase in yield for these runs over those from straight polyforming the incremental effect of propane was determined. In other runs mixtures of propane and propene were charged as outside gas and the incremental yield due to propene could thereby be evaluated. Similarly, incremental yields for butanes and butenes were determined. It is these incremental yields that are shown in Figs. 2 and 3.

Yields for butanes and butenes are based on relatively few runs, so these relations cannot be used with as great assurance as those for propane and propene. They are included as tentative relations pending more complete pilot

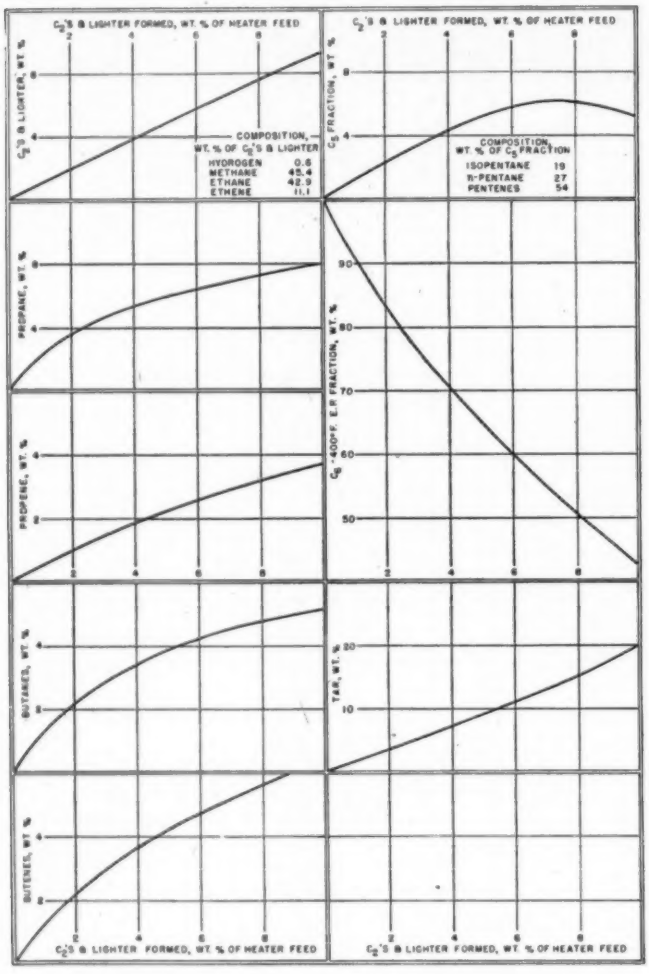


Fig. 1 (left)—Yields from Eastern Venezuela Naphtha charge at 1500 psi pressure

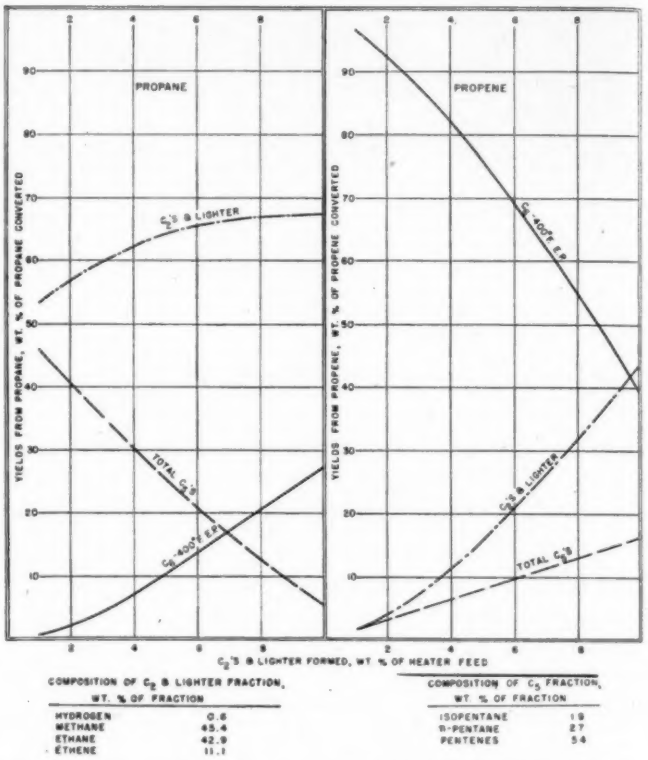


Fig. 2 (above)—Yields from propane and propene at 1500 psi pressure

plant data which are now being obtained. The following averaged yields from butanes are being used at present for all values of severity index:

	Wt. % of Butanes Converted
C_2's and Lighter	32.5
C_5 Fraction	16.6
C_6-400° F. E.P. Fraction	50.9

In making the yield studies on butanes, it was found that the butanes go through intermediate products in being converted to the final products tabulated above. The amounts of these intermediate products, propane and propene, are shown in Fig. 4. These must be taken into account in calculating heater circulation rates but not in calculating ultimate yields.

It was found that the composition of the "C_2's and Lighter" and C_5 fractions, for all operations studied, could be satisfactorily represented by the following averaged values:

	Wt. % of "C_2's and Lighter" Fraction
Hydrogen	0.6
Methane	45.4
Ethane	42.9
Ethene	11.1

	Wt. % of C_5 Fraction
iso-Pentane	19
n-Pentane	27
Pentenes	54

The relationships employed in calculating yields from the Polyform Process are given in Figs. 1 to 3, inclusive. A sample calculation is shown in Table 2. Fig. 1 gives the yields of various components from Eastern Venezuela naphtha at 1500 psi as a function of wt. % "C_2's and Lighter." At any given severity the yields from the naphtha alone are set down in a calculation sheet similar to Table 2. The amounts of various components charged are also set down. Components such as propane, propene, butanes, and butenes charged to the process are added to the amounts of those components

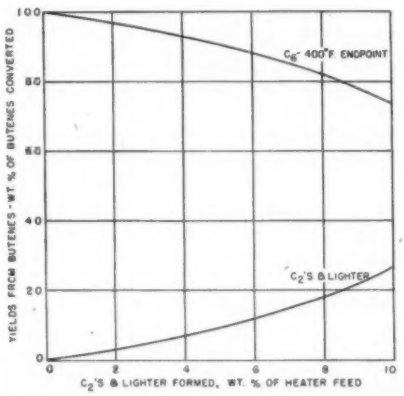


Fig. 3—Yields from butenes at 1500 psi pressure

made from the naphtha to give the total present. From this total are subtracted the amounts of these components leaving the process in the gas and polyform distillate, giving the amount converted. From the amount of each component converted and the yields in Figs. 2 and 3, the yields of various products from C_2 and C_4 fractions are determined and added to those from the naphtha. Thus it is seen that the calculation of a polyform yield by this procedure is as simple as making a material balance. Complete yields for a wide variety of polyform conditions can be readily calculated.

Yields on a wt. % basis have been used in preference to the more conventional vol. % basis because of the much greater convenience in making the calculations.

The accuracy of the yield calculation procedure is shown by the following tabulation of average deviations for 110 pilot plant runs:

	Average Deviation as Wt. % of Naphtha Charge
Hydrogen	±0.016
Methane	±0.69
Ethane	±0.76
Ethene	±0.38
C_2's & Lighter	±1.03
iso-Pentane	±0.38
n-Pentane	±0.41
Pentenes	±0.85
Total C_5 Fraction	±1.13
C_6-400° F. E.P. Fraction	±2.46
Tar	±1.72

No deviations are shown for propane, propene, butanes and butenes, because

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Fig. 1793—125-pound Iron Body Bronze Mounted Gate Valve with flanged ends, outside screw rising stem, bolted flanged yoke, bronze seat rings and taper wedge solid disc. Also available in All Iron.

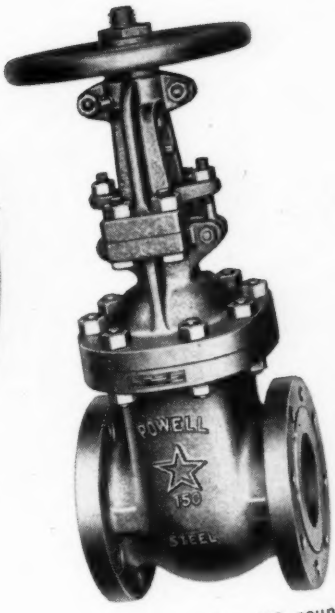

Fig. 1503—Class 150-pound Cast Steel Gate Valve. Has flanged ends, outside screw rising stem, bolted flanged yoke and taper wedge solid disc.

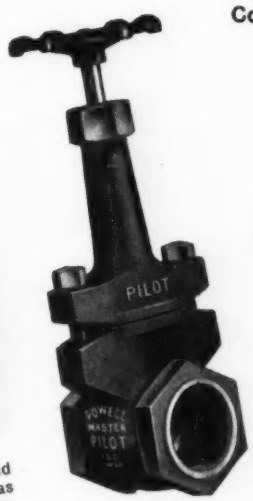

Fig. 1460—Iron Body Bronze Mounted "Master Pilot" Gate Valve. Screwed ends, rising stem, bolted flanged bonnet and taper wedge solid disc. Also available in All Iron.

Fig. 3003—Class 300-pound Cast Steel Gate Valve. Has flanged ends, outside screw rising stem, bolted flanged yoke and taper wedge solid disc.

Fig. 190—150-pound Iron Body Bronze Mounted "Irenew" Globe Valve. Has screwed ends, union bonnet and regrindable, renewable wear - resisting "Powellium" nickel-bronze seat and disc.

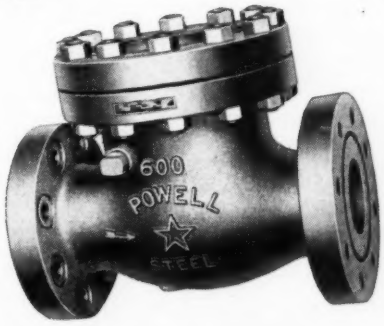

Fig. 6061—Class 600-pound Cast Steel Swing Check Valve with Ring Type Joint End Flanges.

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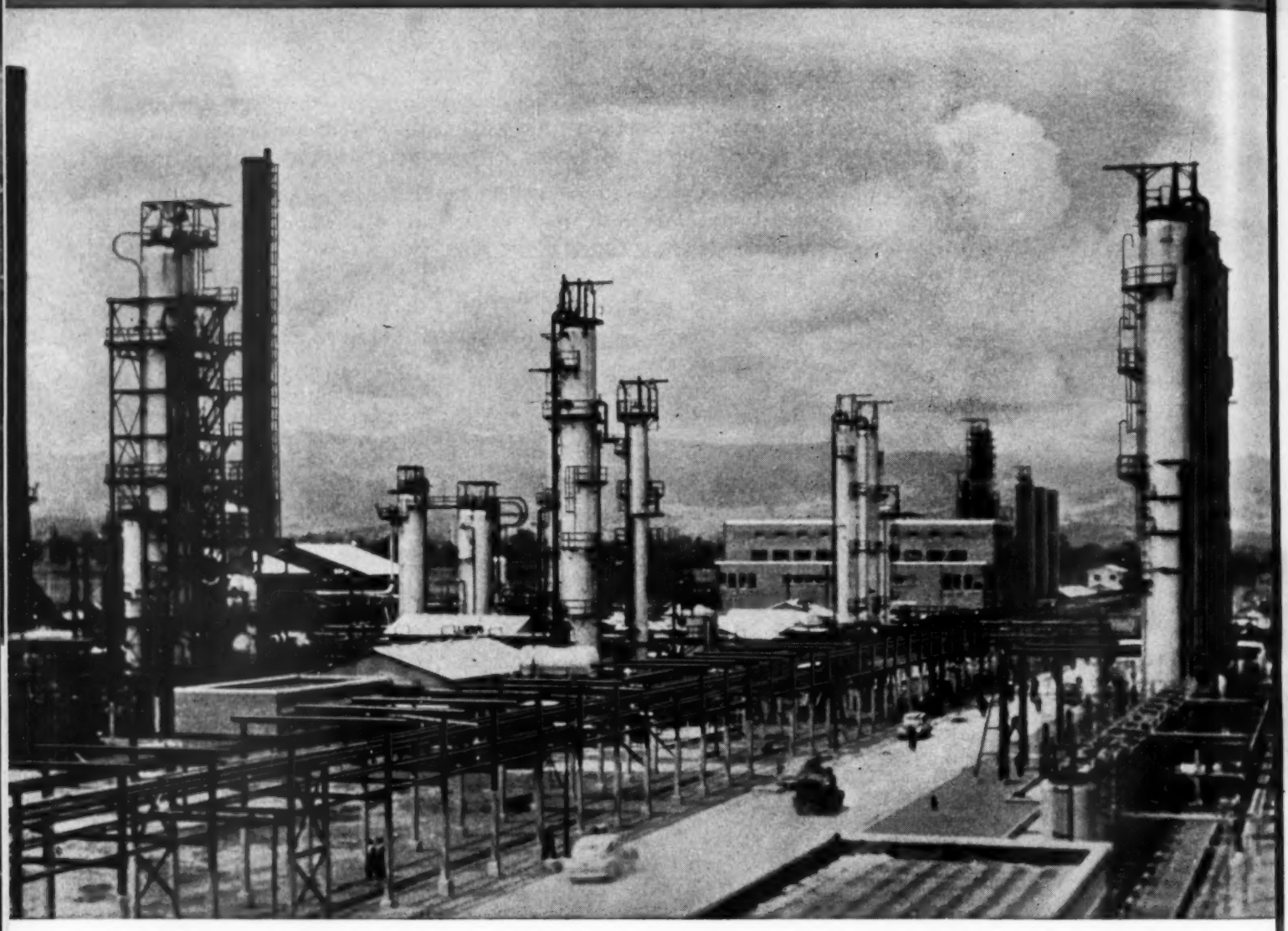

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Doubling of crude oil pumping facilities from Poza Rica to Mexico City.

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TABLE 2—Yield Calculation Sheet, Showing Sample Calculations When Polyforming Eastern Venezuela Naphtha, With and Without the Addition of Outside Gas

Wt % of naphtha charge, except where noted

DESCRIPTION and CONDITIONS of OPERATION	COMPONENT	AMOUNT CHARGED	AMOUNT MADE FROM NAPHTHA	TOTAL	NET YIELD	AMOUNT CONVERTED	C_2's and LIGHTER: HYDROGEN	METHANE	ETHANE	ETHENE	TOTAL: WT% OF COMPONENT	TOTAL: WT% OF NAPHTHA CHG.	PROPANE	PROPENE	BUTANES	BUTENES	C_5 FRACTION: ISOPENTANE	PENTANE	PENTENES	TOTAL: WT% OF COMPONENT	TOTAL: WT% OF NAPHTHA CHG.	C_5 to 400°F: WT% OF COMPONENT	WT% OF NAPHTHA CHARGE	TAR	CIRCULATIONS: CONVERSION PER PASS	CIRCULATION WT% OF NAPHTHA	DENSITY of NAPHTHA CONS. of COMPONENT	CIRCULATION VOL.% of NAPHTHA
							Composition* of fraction, wt%										Composition,* wt%												
							0.6	45.4	42.9	11.1							19.0	27.0	54.0										
Run	Naphtha	100.0										5.7	6.4	2.6	4.2	4.7					5.7		59.7	11.0					
Stock E. Veney.	Propane		6.4	6.4	0.6+	5.8					65.6	3.8								20.7	1.2	13.7	0.8		11.4	49.5	4.556	6.83
K 11.67	Propene		2.6	2.6	0.3+	2.3					20.7	0.5								9.8	0.2	69.5	1.6		27.0	5.9	1.509	8.9
Pressure 1500 psi.	Butanes		4.2	4.2	3.8++	0.4					32.5	0.1								16.6	0.1	50.9	0.2					
X 6.0	Butenes		4.7	4.7	4.2++	0.5					11.8	0.1								0	0.0	88.2	0.4					
	Misc. chg.																											
Straight	Total	100.0					0.1	4.6	4.4	1.1		10.2	0.6	0.3	3.8	4.2	1.4	1.9	3.9		7.2		62.7	11.0				
Polyforming																												
Run	Naphtha	100.0										5.7	6.4	2.6	4.2	4.7					5.7		59.7	11.0				
Stock E Veney	Propane	19.9	6.4	21.3	2.1+	19.2					65.6	12.6								20.7	4.0	13.7	2.6		11.4	162.1	1.556	252.5
K 11.67	Propane	22.2	2.6	24.8	2.5+	22.3					20.7	4.6								9.8	2.2	69.5	15.5		53.0	39.5	1.509	59.6
Pressure 1500 psi.	Butanes	0.3	4.2	4.5	4.0++	0.5					32.5	0.2								16.6	0.1	50.9	0.2					
X 6.0	Butenes	0.4	4.7	5.1	4.6++	0.5					11.8	0.1								0		88.2	0.4					
Polyforming	Misc. chg.	0.9							0.9			0.9																
With Addition	Total	138.7					0.1	10.5	10.9	2.6		24.1	2.1	2.5	4.0	4.6	2.3	3.2	6.5		12.0		78.4	11.0				
of Outside																												
C_3 Fraction																												

X, severity index, C_2's and lighter formed, wt% of heater feed

* These compositions are the average distributions observed in the pilot plant data

+ Based on 90% C_3 Recovery

++ Based on 10% C_4 Recovery

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net yields of these compounds cannot be predicted from the correlation alone. These are recycled in the Polyform Process and in most operations represent both charge and products. Yields of these compounds depend not only on the reaction coil but to an even greater extent on the design and operation of the gas recovery equipment. Thus the net yields of propane, propene, butanes, and butenes can be varied between zero and the total amount of each of these components charged and made from the naphtha, by changing the degree of recovery in the stabilizer and absorber.

Required Circulation of Components

Figs. 5 to 8, inclusive, present relationships between the conversion per pass, γ, of propane, propene, butanes and butenes and the severity index. From these relations, the required amount of each component, c, in the heater feed, per unit of naphtha charge, can be calculated with the aid of the following equation:

$$\gamma = \frac{P + b + g - e}{P + b + c}$$

Where

γ = Conversion of any given component per pass (wt. fraction of component charged and made).

P = Amount of component made from the naphtha, read from Fig. 1.

b = Amount of component made from butane, calculated from Fig. 4. (Applies only to calculation of C_3's circulated).

g = Amount of component charged as outside gas, expressed as wt. % of naphtha charge.

e = Net yield of component eliminated from the unit, expressed as wt. % of naphtha charge. This is dependent on operation of gas recovery equipment.

c = Rate of circulation, i. e. heater feed rate, of the particular component expressed as wt. % of naphtha charge.

Sample calculations are given in Table 2.

Fig. 5 presents the conversion per pass factor, γ, for propane as a function of the severity index. Using the above equation together with Fig. 5, it is possible to calculate the required propane circulation within an average deviation of ±11.8 wt. % (basis naphtha charge).

Fig. 6 presents the conversion per pass factor, γ, for propene in nomograph form as a function of severity index, operating pressure, and the olefin concentration of the outside C_3 fraction charged plus that made from naphtha. This relationship permits calculation of required propene circulation within an average deviation of ±4.6 wt. % (basis naphtha charge).

Fig. 7 gives the conversion per pass factor, γ, for butanes, and Fig. 8 gives this factor for butenes as a function of "C_2's and Lighter." Like the corresponding yield values these relations are only tentative, pending more complete data.

Octane Number

Figs. 9 and 10 give the CFR motor and research octane numbers of polyform gasoline produced from Eastern Venezuela naphtha as functions of the "C_2's and Lighter" severity index and the weight ratio, α, of propane in the heater feed to the total propane plus naphtha in the heater feed.

The effect of propane circulation in raising octane numbers is one of the in-

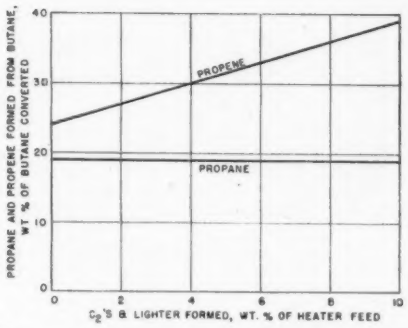

Fig. 4—Intermediate yields of propane and propene from butanes

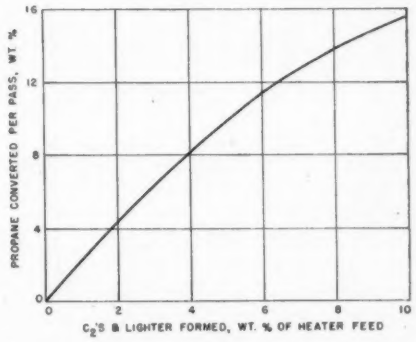

Fig. 5—Propane converted per pass

teresting features of the Polyform Process. Taking a propane ratio of zero to correspond to thermal reforming, it will be seen that at a propane ratio of 0.65, corresponding to polyforming with 16 wt. % outside propane (basis naphtha charge), the CFR M and CFR R octane numbers are approximately 4.0 and 8.0 points higher, respectively, at the same severity. Actually, the over-all advantage is greater than this because the presence of circulated propane permits

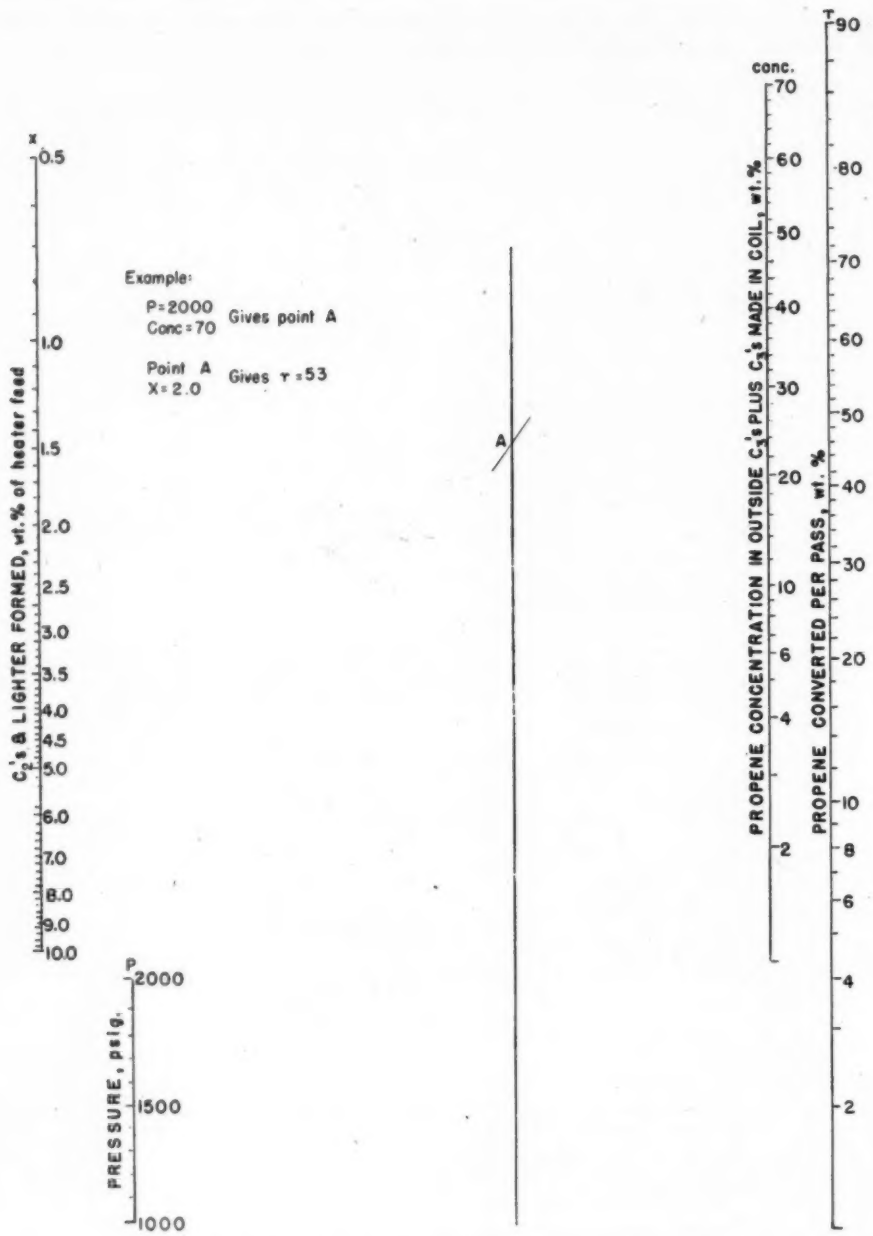

Fig. 6—Nomograph for conversion per pass of propene

operating at greater severity without coking and increased gasoline yields are obtained, amounting to some 35 wt. % of the propane converted.

By taking account of the charge octane number and characterization factor it has been possible to generalize the relationships of Figs. 9 and 10 to cover a wide range of naphtha charge stocks. The average deviation of observed values from those predicted by these generalized expressions is ±1.09 CFR M octane numbers and ±1.48 CFR R octane numbers.

Using Eastman's method[1] together with these octane expressions it is possible to calculate the leaded octane numbers of polyform gasoline containing up to 3 cc. of TEL per gal, within an average deviation of ±1.07 CFR M and ±1.34 CFR R octane numbers. Eastman's method correlates a lead response factor, Θ, with wt. % sulfur by the lamp method and the clear octane number sensitivity (CFR R minus CFR M) of the gasoline.

Correlation of Severity Index

Having found that "C_2's and Lighter" formed per pass was an index of severity of treatment which could be correlated with yields, octane numbers and required heater circulation rates, the final steps comprised tying this index to operating conditions. This was done through a procedure for calculating conversion per pass and pressure drop in tubular reaction coils, which has been previously described[2].

As brought out in Reference 2 this method involves determining reaction velocity constants from laboratory pilot plant runs and then using these constants to calculate the amount of conversion that will take place in a proposed commercial reaction coil. A plot was presented which correlates reaction velocity constants from polyforming runs with the weight ratio, α, of propane in the heater feed to the sum of propane plus naphtha, and the aniline point of the naphtha charge. The average deviation of the reaction velocity constants from this plot is ±11%.

When "C_2's and Lighter" formed is used as a measure of the severity of thermal treatment the reaction velocity constant is relatively independent of charging stock. For example, the value for propane at 800° F. is 3×10^{-6} whereas that for 23° API topped East Texas crude at the same temperature is only 9×10^{-6}. This difference is much smaller than when reaction velocity is expressed in terms of material decomposed. On this basis "C_2's and Lighter" would be the main products in cracking

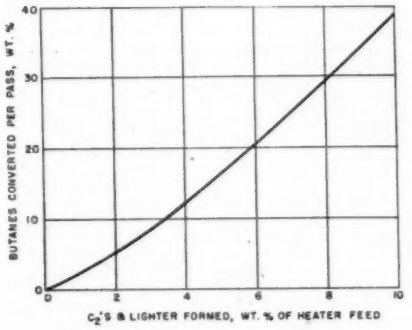

Fig. 7—Butanes converted per pass at 1500 psi pressure

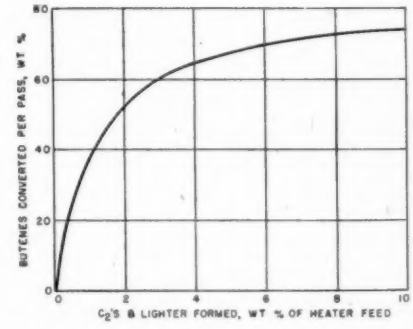

Fig. 8—Butenes converted per pass at 1500 psi pressure

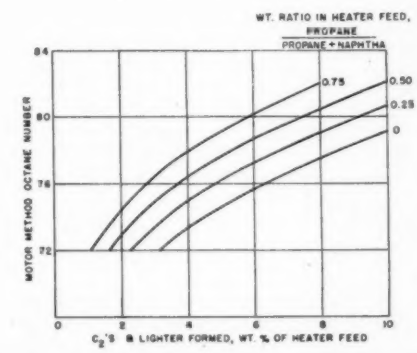

Fig. 9—CFR Motor octane number of 10 RVP gasoline

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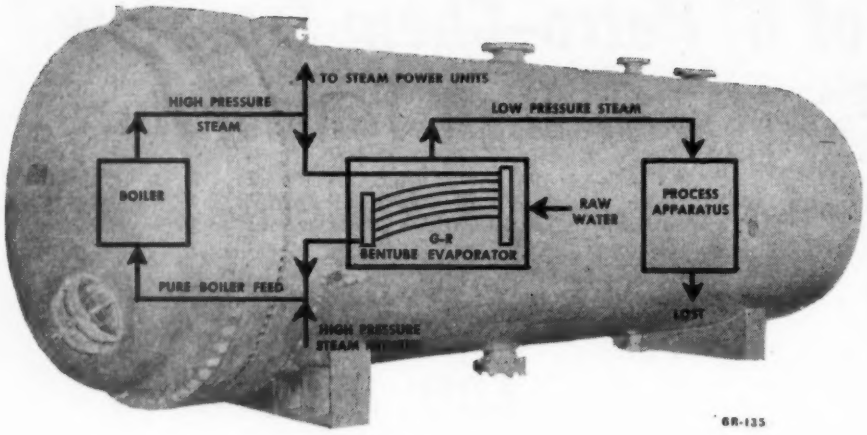

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Correlation of Variables

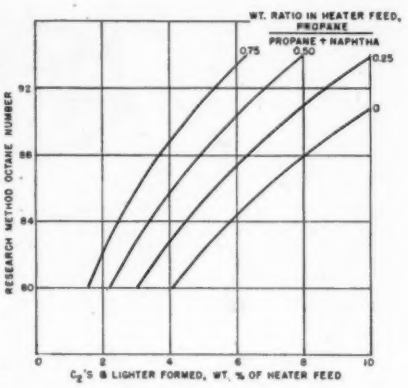

Fig. 10—CFR Research octane number of 10 RVP gasoline

propane and the constant would still be about 3×10^{-6}. However, gas and gasoline would be the major decomposition products from topped East Texas crude and "wt. % gas plus gasoline formed" would be the conventional index for expressing cracking. Here the reaction velocity constant would be about 240×10^{-6} or 80 times that of propane. Thus while high boiling stocks such as topped crudes crack to gas and gasoline at relatively high rates they still form "C_2's and Lighter" at roughly the same rate as lower boiling stocks. Reaction velocity constants based on "C_2's and Lighter" are independent of operating pressure.

Preliminary studies indicate that the procedures illustrated in this paper can also be applied to gas oil polyforming operations. Thus it would appear that the correlation methods employed are sufficiently fundamental to cover a fairly wide range of problems and that "C_2's and Lighter" may be a promising new instrument for correlating yields, product characteristics and operating conditions in thermal conversion operations.

References

(1) Eastman, *Ind. Eng. Chem.*, 33, 1555 (1941).
(2) Hirsch, Crawford, and Holloway, *Ind. Eng. Chem.*, 38, 885 (1946).
(3) Smith and Watson, *Ind. Eng. Chem.*, 29, 1408 (1937).

Correction, Please

Our attention has been called to two errors which appeared in the December, 1946, issue of Petroleum Processing. In "Polyform Process Utilizes Excess Gases in Upgrading Naphthas and Gasolines," pg. 244, the statement regarding royalty should have said that it will be "of the order of $7.50 per barrel of daily furnace throughput capacity," not "per barrel of daily throughput capacity."

In "Naphtha Polyforming," pg. 272, Fig. 6, the values from 8 to 61 in the center grid represent the octane number of the charge.

Petroleum Technologists in the Headlines

Mr. Jackson

Mr. Sheldon

R. Rea Jackson has been appointed manager of the Paulsboro, N. J., refinery of the Socony-Vacuum Oil Co. He succeeds **Howard W. Sheldon** who has been transferred to the company's headquarters in New York City to become assistant director of Socony-Vacuum laboratories.

Mr. Jackson has been general superintendent of the Beaumont, Texas, refinery of the Magnolia Petroleum Co., an affiliate of Socony-Vacuum, for the last ten years. He joined Magnolia as a chemist in 1923 following his graduation from the University of Texas.

Mr. Sheldon was graduated from the University of Michigan in 1917 and joined Socony-Vacuum as an engineer at Paulsboro refinery in 1926. In 1929 he was transferred to New York and became chief chemical engineer of the Research and Development department. Four years later he returned to Paulsboro as chemical engineer and in 1943 became general manager of the refinery.

* * *

C. R. Johnson, former Lt. Com. in the U. S. Navy is now on the engineering staff for Shell Oil Co., San Francisco.

* * *

M. I. Moyer has returned as chemist at the Tallant, Okla., division of Cities Service Oil Co., after being in the service.

* * *

Franklin G. Wilson has joined the API as assistant to David V. Stroop, director of the department of Safety. He will be stationed temporarily in the Washington office.

Mr. Wilson was with the government's Air Transport Service in a civilian capacity, was with PAW during part of the war, and previously was with Cities Service Oil Co. and Gulf Oil Co.

* * *

Robert Matteson, supervisor in charge of the analytical division of the Richmond Laboratories of California Research Corp., a Standard of California subsidiary, has been elected chairman of the California Section of the American Chemical Society for 1947. He succeeds **Dr. Louis B. Howard** of the U. S. Department of Agriculture.

Other new officers of the Section include **George M. Cook,** California Research Corp., secretary, and **Fred D. Tuemmler,** Shell Development Co., treasurer.

Mr. Matteson has been active in the development of science and industry on the Pacific Coast and was instrumental in organizing the Pacific Coast Exposition. He holds a B.S. in Mechanical Engineering from the University of California at Berkeley and was formerly on the research staff of Standard Oil Co. of California.

* * *

Karl Beaver, a former Lt., in the U. S. Navy Bureau of Aeronautics is now connected with Ethyl Corp., Detroit.

* * *

Samuel H. Lee, Jr., formerly with Shell Oil Co., is now assistant professor of chemistry at the University of Texas, Austin.

* * *

Beginning Jan. 1, 1948, **Dr. Charles Allen Thomas** will take office as president of the American Chemical Society. He is a vice president and technical director of the Monsanto Chemical Co. and one of the key figures in the development of atomic energy.

Dr. Thomas

Dr. Thomas received the Medal of Merit from the War Department for his services during the recent war. He was the leader in developing catapult rockets and other types of rocket propelled missiles.

Born in 1900 Dr. Thomas was graduated from Transylvania College and M.I.T. with degrees of B.A., M.S., and Sc.D. In 1923 he joined the General Motors Research Corp. as a research chemist. His work resulted in the production of tetra-ethyl lead. Later, he was transferred to the Ethyl Gasoline Corp. as a research chemist. In 1926, together with Dr. C. A. Hochwalt, he organized the Thomas and Hochwalt Laboratories at Dayton, Ohio, and specialized in consulting and research work for industrial concerns. In 1936 the laboratories were taken over by Monsanto Chemical Co. and Dr. Thomas became central research director of the company.

At Monsanto, Dr. Thomas centered his work on the production of synthetic resins from petroleum hydrocarbons and formation of diolefins, olefins and aromatics by the pyrolysis of hydrocarbons, plastics and synthesis of various aliphatic compounds.

Author of numerous scientific papers and holder of many patents, Dr. Thomas became a vice president of Monsanto in April, 1945.

* * *

Per K. Frolich, a past president of the American Chemical Society, has been appointed to the newly created post of coordinator of research for Merck & Co., Inc., Rahway, N. J. He comes to Merck from Standard Oil Development Co. of New Jersey, where he was director of the chemical division of Esso Laboratories.

* * *

Honorably discharged from the Navy, **Harry F. Hostetler** is now fuels and lubricants engineer with Standard Oil Co. of Ohio at Cleveland.

* * *

F. C. Buckwalter was elected chairman of the Kansas Society of Petroleum Engineers at its December meeting. He is with Shell Oil Co.

Also with Shell and elected along with Mr. Buckwalter was **R. G. Daley,** secretary-treasurer.

* * *

J. Paul Ratliff, Jr., engineer for Humble Oil and Refining Co. at Crowley, La. has been transferred to New Orleans.

* * *

Urban M. Warren, formerly foreman at Long Beach, Calif. has been transferred as a foreman to the Bakersfield plant of Shell Oil Co.

* * *

Lawrence O'Donnell has been promoted to regional chief mechanical engineer of Shell Oil Co., Inc., in Houston. The regional staff coordinates activities and acts in advisory and consultant capacities for the areas east of the Rockies. **W. S. Crake** has been promoted to chief mechanical engineer for the Houston area. Other new offices are located in Midland, New Orleans and Tulsa.

* * *

Max W. Ball has been named for the appointment of director of the Oil and Gas Division, Department of the Interior. He will succeed Ralph K. Davies, the now acting director.

Mr. Ball started his career of public service with the U. S. Geological Survey in 1906 after receiving his degree from the Colorado School of Mines. In four years he became head of the Oil Board and held that position until 1916 when he became mining engineer and law officer for the Bureau of Mines.

In 1944 Mr. Ball became special assistant to Mr. Davies who was deputy petroleum administrator for war. He was recently associated with the Michigan Consolidated Gas Co.

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Personals

Morris Evans Leeds, founder and chairman of the board of Leeds & Northrup Co., Philadelphia, received the A.S.M.E. Medal of the American Society of Mechanical Engineers recently "because of outstanding achievements in the invention and development of electrical and temperature measuring instruments, and in the field of industrial relations." He is the inventor of the "Leeds mechanism", a basic element in automatically-operated, balanced-current recording and controlling instruments for industrial use.

His achievements in the field of industrial relations include noteworthy liberal management policies in the company he founded. Mr. Leeds retired as president of Leeds & Northrup Co. in 1939 and has since been president of the Philadelphia Board of Education.

° ° °

Standard Oil Development Co. has named **Dr. William J. Sparks** director of the chemical division of Esso Laboratories, replacing Dr. Per K. Frolich, who has resigned after 11 years with the company. With **Robert M. Thomas** now at the company's Baton Rouge laboratory, Dr. Sparks developed Butyl shortly before the war.

Dr. Sparks

A 41-year-old native of Wilkinson, Indiana Dr. Sparks was graduated from the Univesity of Indiana in chemistry with bachelor's and master's degrees and received his doctor's degree at the University of Illinois.

In 1936 he joined Standard Oil Development Co. as a research chemist, aiding since in the development of new uses for petroleum products. In 1939 he was principal chemist of the U. S. Department of Agriculture in charge of oil and protein development in Bureau of Agricultural and Industrial Chemistry. He returned to the development company in 1940, becoming assistant director of the chemical division in 1943, and associate director in 1945.

° ° °

Two oil men have been elected to serve on the board of six directors for the American Institute of Mining and Metallurgical Engineers for the coming year. They are **John R. Suman,** vice president of the Standard Oil Co. (N. J.) and **C. V. Millikan,** chief production engineer for the Amerada Petroleum Corp., Tulsa.

° ° °

C. R. Inglis has returned to his old job as production engineer at Cities Service Great Bend, Kans., plant after being discharged from the service.

Personals

H. C. Lawton has accepted a position as senior chemist with the research and development department of Atlantic Refining Co. Philadelphia, where he will carry out studies on petroleum production technology. He comes from the Pennsylvania Grade Crude Oil Assn.'s production research laboratory.

* * *

Terence Bredin, John Clougher, John Hafner and **Edward Mooney** have been appointed refinery foremen at Standard of New Jersey's Bayonne plant.

* * *

Roman L. Sailer has been promoted from acting chief engineer to chief technical service engineer for the Freedom-Valvoline Oil Co., East Butler, Pa.

* * *

R. L. Swoope, engineer at Universal Oil Products Riverside, Ill., plant has been transferred to Berwyn, Ill.

* * *

Thomas Brownfield has been transferred to Tulsa as assistant to Oscar Schorp, president of the Carter Oil Co. Replacing Mr. Brownfield as special assistant to the coordinator of producing activities for Standard Oil Co. (N. J.) is **M. A. Wright. R. P. Walters** replaces Mr. Wright in New York.

* * *

Following the recent meeting of the API, **Director E. L. Dalemont** and his assistant, **J. de Courlon,** of the French Petroleum Industry Buying Agency of New York City, and **A. Martin,** technical director of Direction des Carburants, Paris, have been visiting and studying procedures and methods at various oil centers in the Southwest.

* * *

Albert R. Yurgerwitz has been promoted to head pumpman at Standard of New Jersey's Bayway, N. J. refinery.

* * *

L. G. R. Tompkins has recently completed work on his Ph.D. at Purdue, and is now with Humble Oil & Refining Co., Baytown, Texas, as research chemist, doing applied research on petroleum and its products.

Annual Index Ready

The annual index of articles published during 1946 in PETROLEUM PROCESSING (Sept. - Dec.) and the *NPN Technical Section* (Jan.-Aug.), its predecessor, is now ready. It gives a complete subject and author listing of all material appearing during the year in the two magazines. Copies of the index can be obtained, without charge, upon request to the Reader's Service Department of PETROLEUM PROCESSING, 1213 West Third St., Cleveland 13, Ohio.

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Personals

George H. Evans of the Point Breeze refinery of Atlantic Refining Co., has been named foreman of the wax plant. He was formerly senior chemical engineer.

° ° °

M. T. Miller, foreman for Standard of California at Taft has been transferred to Pasadena Calif.

° ° °

The Alberta Petroleum Assn. at its recent meeting in Calgary reelected **F. M. Graham** president for another term.

J. O. Galloway and **F. F. Reeve** were voted in as vice presidents and **E. W. Kolb** was elected secretary-treasurer.

° ° °

Dr. C. C. Crawford has been appointed assistant manager of Phillips Petroleum Co.'s chemical products department. He will be in charge of the special products, product development, and Perco divisions.

Succeeding Dr. Crawford as head of the product development division is **Dr. A. J. Dirksen.**

Dr. Crawford started with the Phillips company in January of 1943 in the special products division having previously been employed as a chemist with Shell Development Co. He was made manager of the products development division in March 1944.

° ° °

F. McDowell has been promoted to foreman in the process department at the Texas City refinery of the Pan American Refining Corp.

° ° °

Howard T. Jayne, safety inspector for the Philadelphia Gas Work Co., has been reappointed chairman of the Accident Prevention Committee of the American Gas Association for the 1946-1947 term.

° ° °

Clarence Norman, foreman at the St. Elmo, Ill., plant of the Carter Oil Co., has been transferred to the marketing department in Tulsa.

° ° °

R. C. McCurdy is being transferred by the Shell Oil Co. to take charge of their Venezuelan operations at Maracaibo. He was division manager at San Joaquin Basin for Shell.

° ° °

Chester F. Smith, a company director, has been appointed a vice president of Standard Oil Co. (N.J.). He has been associated with Standard for the last 35 years in manufacturing and engineering operations.

In 1944 he was named chairman of Standard's coordination committee, a group for the centralization and study of the managements of the subsidiary companies. Until his appointment as a director he was the president of Standard Oil Co. of New Jersey, the main subsidiary of the company.

Special Problems in Binary Distillation

By ROBERT R. WHITE, Associate Professor
and W. T. BOYD, Graduate Student

Department of Chemical and Metallurgical Engineering
University of Michigan

Last month the authors discussed analytical methods that could be used in the design of fractionating towers for calculating the number of theoretical plates required for a separation. The McCabe-Thiele method, Smoker's equation, and the Fenske or Underwood equation were all covered, and illustrated with examples.

This month they discuss a few of the special applications of these techniques, including partial condensers, two-feed and three-feed columns, side streams, side stream recirculation, and low-temperature distillation.

Previous articles in this series discussed the basic theory of binary distillation. Future articles will take up the design of towers, as well as multiple component, azeotropic and crude oil distillation.

THE following discussion considers a few special problems which may arise in the application of the techniques previously described (PETROLEUM PROCESSING, Dec., 1946 pg. 319).

Partial Condensers

Where a partial condenser is used, only a portion of the vapors, sufficient to form the reflux liquid, are condensed, and the distillate product is withdrawn as a vapor, the receiver functioning as a vapor-liquid separator. The enthalpy-composition diagram for this operation is shown in Fig. 1.

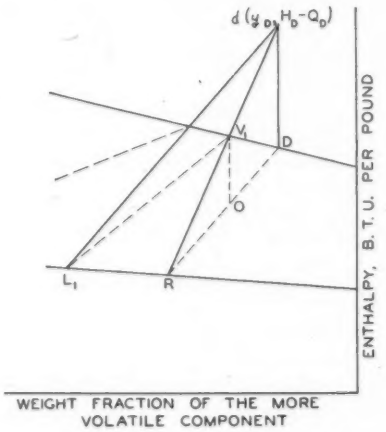


Fig. 1—Enthalpy-composition diagram where a partial condenser is used

The coordinates of the difference point, d, for the rectifying section are unchanged, i.e., (y_D, $H_D - Q_D$). The reflux liquid, R, where it is in equilibrium with the distillate product, is located on the liquid saturation line at the end of the equilibrium tie line from the distillate product, D, on the vapor saturation line, and the points V_1, R and d lie on a straight line. The point O, which represents the sum of the reflux liquid and the distillate product, lies directly below the point V_1. The reflux ratio R/D is equal to the ratio of the distances OD/RO, or dV_1/V_1R.

Two-Feed Columns

The calculation of plate requirement in two-feed columns may be explained most conveniently by reference to Example 6, the solution to which is shown by Fig. 2.

Example 6:

It is desired to separate 258 lbs./hr. of a feed, F_1, having zero enthalpy and containing 74.0 wt. % ethanol, balance water, and 742 lbs./hr. of a feed, F_2, having an enthalpy of 702 Btu/lb. and containing 47.1 wt. % ethanol, balance water, into two products containing 90.0 and 1.0 wt. % ethanol. The heat supplied to the still will be 386 Btu/lb. of combined feed. The reflux liquid and distillate product will have an enthalpy of 50.0 Btu/lb. How many equilibrium plates must be provided in the column?

Points F_1 and F_2 in Fig. 2 represent the two feeds. Point O is the addition point for the two feeds and is located on the line F_1F_2 so that the ratio of the distances

$$OF_2/OF_1 = F_1/F_2 = 258/742$$

The energy added in the still per pound of combined feed is represented by the distance OO' (386 Btu/lb.), the point O' representing the combined feeds plus the energy added in the still per pound of ($F_1 + F_2$). The point O' represents also the sum of the bottom product, B, and the distillate product minus the energy added in the condenser, d, (x_D, $h_D - Q_D$). The difference point for the rectifying section, d, is located by extending the line BO' to the value $x_D = 0.90$. The difference point for the stripping section, d', is located by extending the line dO to the value $x_B = 0.01$.

It is now possible to begin the plate to plate construction for the rectifying section. If this construction is continued until the line dOd' is passed, and continued by using the point d' the result is the number of plates required if the two feeds were combined and introduced on the same plate.

The difference between the vapor and liquid passing one another in the middle section of the column between the two feed plates equals the difference between the upper feed, F_1, and the distillate product minus the energy added in the condenser. It also equals the difference between the lower feed, F_2, and the bottom product minus the energy added in the still. Therefore, the difference point for the middle section, d'', is located at the intersection of the line dF_1 with the line $d'F_2$.

The plate to plate construction for the rectifying section is carried out using point d, until the plate is reached which has an ethanol concentration in the liquid less than that indicated by the intersection of the line dF_1 with the liquid saturation line. The feed, F_1, is introduced on this plate. The construction is carried out below the upper feed plate using the point d'' until the plate is reached which has an ethanol concentration

in the liquid less than that indicated by the intersection of the line $d'F_2$ with the liquid saturation line. The feed, F_2, is introduced on this plate. The remainder of the column is calculated by using the point d' in the ordinary manner for stripping sections.

As indicated in Fig. 2, nine plates are required for the specified separation. The feed F_1 should be introduced on plate 5, and feed F_2 on plate 7.

It should be pointed out that in some cases the lines dF_1 and $d'F_2$ are parallel. This condition arises when the quantity of liquid in the section between the feed plates equals the quantity of vapor.

Three Feed Columns

The graphical construction used to determine the difference points for the four sections of a three-feed column is shown in Fig. 3. The three feed streams are represented by the points F_1, F_2, and F_3. The combined feed is represented by point O, the addition point for F_1, F_2 and F_3. Points d and d' are the difference points for the rectifying and stripping sections of the column, respectively. The difference between the vapor and liquid passing one another in the section below the rectifying section equals the difference between the upper feed, F_1, and the distillate product minus the energy added in the condenser, represented by the point d. It also equals the difference between the sum of the feeds F_2 and F_3, represented by point O_{23} and the bottom product minus the energy added in the still, represented by point d'.

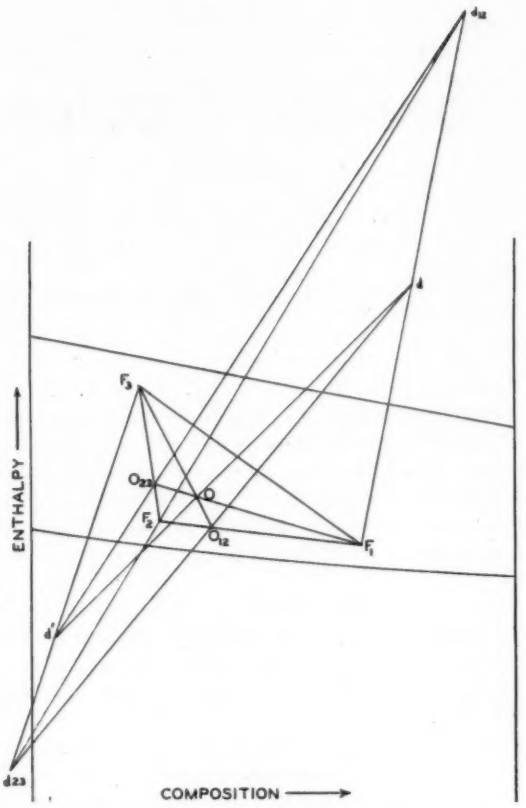


Fig. 3—Graphical construction used to determine the difference points for the four sections of a three-feed column

Therefore, the difference point for this section is located at the intersection of the line dF_1 and the line $d'O_{23}$ where O_{23} is the addition point for the feeds F_2 and F_3. Similarly, the difference point for the section above the stripping section is located at the intersection of the line $d'F_3$ and the line $O_{12}d$, where O_{12} is the addition point for the feeds F_1 and F_2.

Side Streams

The calculations for a column from which a side stream product is withdrawn are identical to those for a two-feed column, since the side stream is equivalent to an additional feed stream with the flow reversed.

The graphical solution to Example 7 is shown in Fig. 4.

Example 7

It is desired to separate a feed containing 56.0 wt. % ethanol, balance water, and having an enthalpy of 300 Btu/lb., into three products containing 90.0, 70.4, and 1.0 wt. % ethanol. The separation is to be accomplished in a plate column equipped with a still and apparatus for returning reflux. The enthalpy of the reflux liquid and distillate product is to be 60.0 Btu/lb. The heat supplied to the still will be 378 Btu/lb. of feed. The quantity of side-stream product withdrawn is to be 0.290 lbs./lb. of feed. How many equilibrium plates must be provided?

The feed is represented in Fig. 4 by the point F; the side-stream product, which will be a saturated liquid, is represented

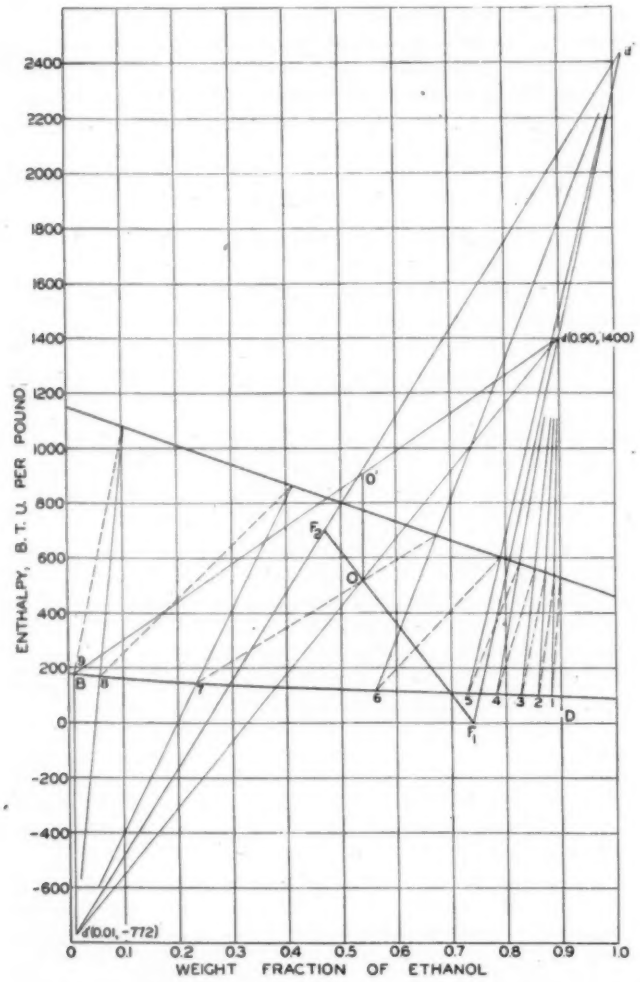


Fig. 2—Enthalpy-composition diagram used in plate calculation two-feed columns as given in Example 6

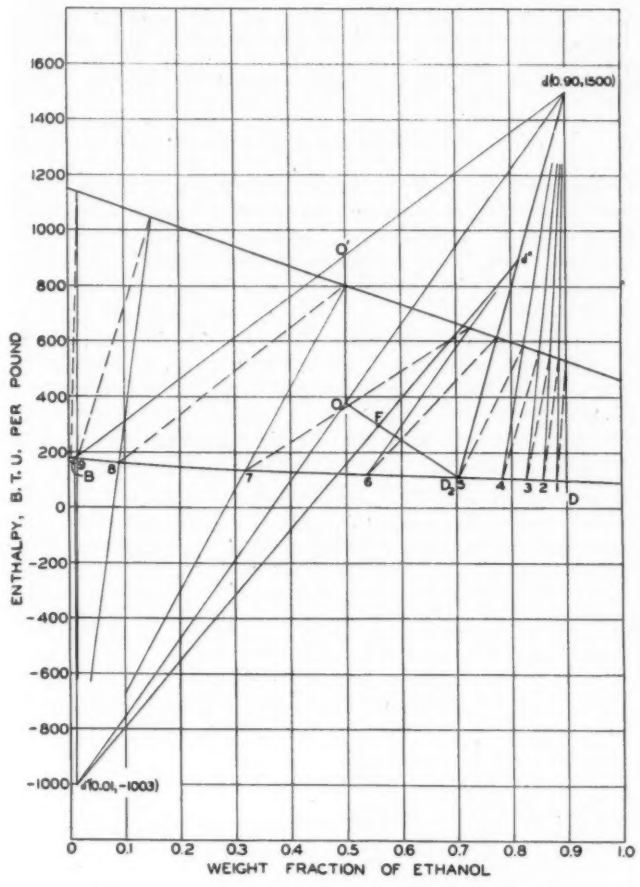


Fig. 4—Enthalpy-composition chart used in Example 7, for calculations for a column from which a side stream product is withdrawn. The determinations are identical to those for a two-feed column because the side stream is equivalent to an additional feed stream with the flow reversed

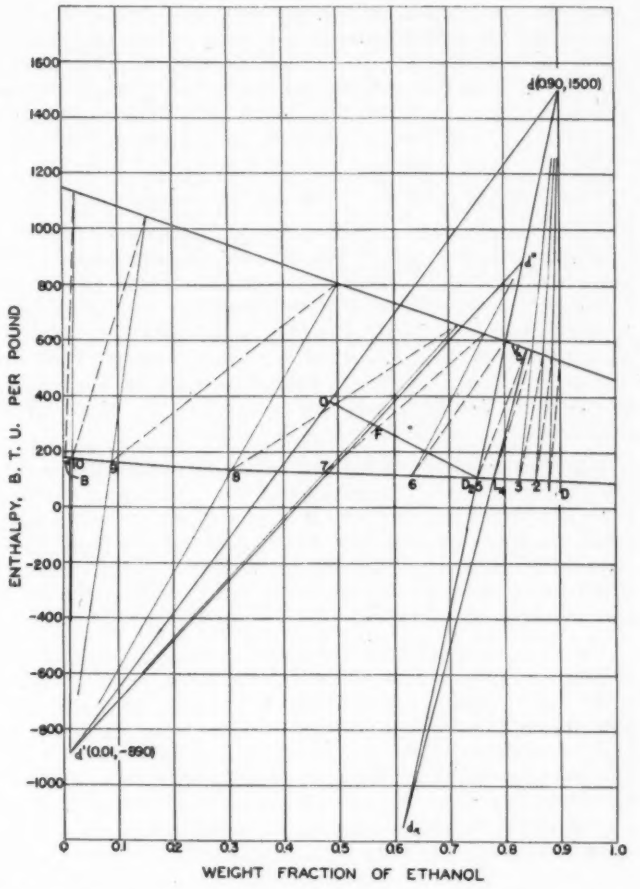


Fig. 5—Graphical solution to Example 8, involving side stream recirculation

by the point D_2 located on the liquid saturation line. The point O is difference point for the feed and side stream and is located on the line FD_2 so that the ratio of the distances, OF/OD_2, = 0.290.

The heat supplied to the still is 378 Btu/lb. of feed or 378/(1.0 − 0.290) = 532 Btu/lb. of feed less side stream, $F - D_2$. The energy added in the still per pound of feed less side stream is represented by the distance OO' (532 Btu/lb.), and the point O' represents the sum of the feed less the side stream and the energy added in the still per pound of feed less side stream. Point O' also represents the sum of the bottom product, B, and the distillate product minus the energy added in the condenser. Thus the difference point, d, for the rectifying section is located by extending the line BO' to the value x_D = 0.90. The difference point d' is located by extending the line dO to the value x_B = 0.01. The point, d'', which represents the difference between the liquid and vapor passing one another in the section between the draw-off plate and the feed plate, is located at the intersection of the lines dD_2 and $d'F$, since the side stream is withdrawn from a plate above the feed plate. Where the side stream is withdrawn from a plate below the feed plate the point d'' is located at the intersection of the lines dF and $d'D_2$.

The plate to plate construction is carried out as described previously, using the point d for the rectifying section, the point d'' for the section between the feed and draw-off plates and the point d' for the stripping section. As indicated in Fig. 4, 9.4 equilibrium plates are required, the side stream being withdrawn from the fifth plate. The quantity of distillate and bottom products per pound of feed are 0.392 and 0.318, respectively.

Side Stream Recirculation

A problem which is associated with the withdrawal of a side stream is that of controlling side stream composition. When the distillate and bottom product compositions are fixed, one must accept what compositions are available on the plates of the column with the particular reflux ratio being used. For instance, if in illustrative Example 6 it were desired to obtain a side stream containing 75.0 wt. % ethanol while making a 90.0% distillate and a 1.0% bottom product, it would be possible to obtain this product by increasing the reflux ratio until the composition of the liquid on the fourth plate was 75.0% ethanol or by decreasing the reflux ratio until the composition of the liquid on the fifth plate was 75.0% ethanol.

It is also possible to control side-stream composition at reflux ratios where ordinarily no plate of the column has liquid of the desired composition, by recirculating a portion of the side stream to the plate above the draw-off plate. The effect of the recirculation is to divide the column into four sections —the rectifying section, a recirculation section between the draw-off plate and the plate above, a middle section between the feed and draw-off plates, and finally the stripping section.

Example 8

The feed of Example 7 is to be separated into distillate and bottom products containing 90.0 and 1.0 wt. % ethanol, and a side stream containing 75.0% ethanol is to be made,

using the same reflux ratio as was used in Example 6, by recirculating hot side stream to the plate above the draw-off plate. The enthalpy of the reflux liquid and distillate product is to be 60.0 Btu/lb. and the quantity of side-stream product withdrawn is to be 0.290 lbs./lb. of feed. How many plates are required, and how much heat must be supplied to the still?

The graphical solution to Example 8 is shown in Fig. 5.

The point d for the rectifying section will have the same coordinates as in Example 7, Fig. 4, since the reflux ratio is the same. The point O, representing the feed less side stream, is located on the extension of the line FD_2 so that the ratio of the distances $OF/OD_2 = 0.290$. The difference point for the stripping section, d', is located on the extension of the line dO at the value $x_n = 0.01$. The difference point for the section between the feed and draw-off plates, d'', is located at the intersection of the lines D_2d and $d'F$.

The plate to plate construction is carried out for the rectifying section until the composition of the liquid on the fourth plate is determined as 0.779. It is now apparent that an additional plate in the rectifying section will have a liquid composition of less than 0.75 wt. % ethanol. It is necessary, therefore, to recirculate liquid from the fifth plate to the fourth plate and to withdraw the side stream from the fifth plate.

The difference between the vapor and liquid passing one another between the fourth and fifth plates, represented by point d_r, is equal to the difference between the recirculated side stream fed to the fourth plate, represented by point D_2, and the distillate product minus the energy added in the condenser, represented by point d. The point d_r will therefore lie on the line dD_2. It must also lie on the line L_4V_5, where L_4 represents the liquid leaving the fourth plate and V_5 the vapor rising from the fifth plate. The point L_4 is located from the plate to plate construction in the rectifying section and the point V_5 must represent the vapor in equilibrium with the liquid containing 75.0 wt. % ethanol. The point d_r is thus located by the intersection of the lines dD_2 and L_4V_5 and has the coordinates (0.612, −1140).

The ratio of the quantity of liquid recirculated to quantity of the distillate product is equal to the ratio of the distances d_rd/d_rD_2. The ratio of the side stream product to the distillate product is equal to the ratio of the distances dd''/D_2d'' and the ratio of liquid recirculated to the side stream product is equal to the ratio of the distances

$$\frac{d_rd/d_rD_2}{dd''/D_2d''} = 2.64.$$

The material balance on the basis of one pound of feed gives the following values for the quantities of the products: $D_1 = 0.377$; $D_2 = 0.290$; and $B = 0.333$. The quantity of liquid recirculated is 0.766 lbs./lb. of feed. The number of equilibrium plates required is 10. The heat supplied to the still per pound of feed is (890 + 179) (0.333) = 356 Btu.

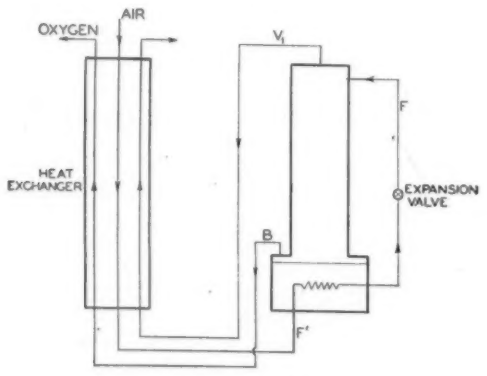


Fig. 6—Diagrammatic sketch for oxygen production by means of Linde liquefier and stripping column. Stripping column is at right, heat exchanger on left

Low Temperature Distillation

The petroleum industry has long used high pressure distillation in fractionation operations producing highly volatile overhead products in order that cooling water could be used to produce reflux. The maximum pressure which may be used depends upon the critical properties of the materials being fractionated.

It is also possible in some cases, such as in the separation of hydrogen, methane, ethylene and ethane from cracked gases, to use the principles of self-refrigeration for producing reflux instead of high pressures. The basic principles of such operations are well illustrated by the methods commonly used to fractionate air.

When air is separated into oxygen and nitrogen it may be considered to be a binary mixture. One operation which produces oxygen as the primary product is illustrated in Fig. 6 and consists of a Linde liquefier and a stripping column. Air at atmospheric temperature and at about 30 atm. pressure enters the heat exchanger where it is cooled by the products

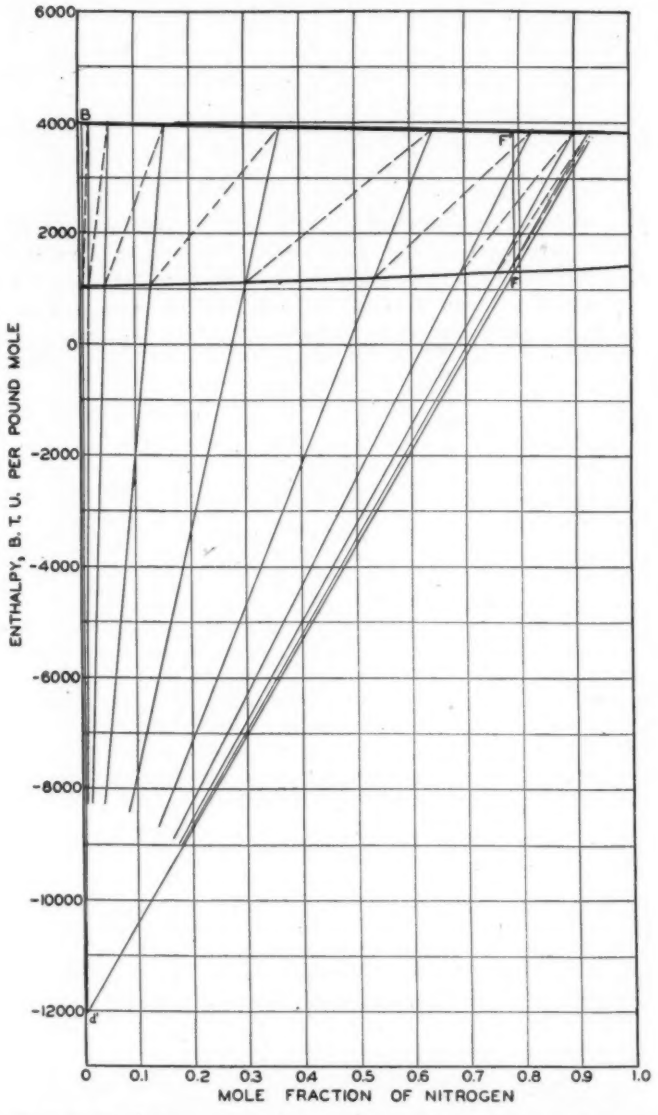


Fig. 7—Enthalpy-composition diagram for nitrogen for use in calculations resulting from equipment shown in Fig. 6

from the stripping column. The cooled air passes through the still where it is cooled further as it furnishes the heat required for operating the column. After passing through the reboiler the air is expanded through the valve to approximately 1 atm. pressure and is introduced to the top plate of the column as a saturated liquid.

This column operates as a stripping column, which has been discussed previously. The enthalpy-composition diagram of Fig. 7 shows the operation of such a column containing an infinite number of plates and producing oxygen containing 0.5 mole % nitrogen, withdrawn as vapor from the still, represented by the point B. The point F represents the expanded air feed and the point F' the air as it enters the still. The overhead vapors represented by point V_1 are in equilibrium with the entering F (because infinite plates are available) and contain 6.3 mole % oxygen. Thus the recovery of oxygen under these conditions is 75.0 mole % and the maximum purity of the nitrogen obtainable is 93.7 mole %.

The low recovery of the desired product is characteristic of stripping columns. In ordinary fractionations, rectifying plates are provided above the feed plate in order to produce a pure overhead product. However, the operation of such rectifying plates demands a supply of relatively pure liquid reflux which in this case must be provided at approximately the temperature of saturated liquid nitrogen at 1 atm. pressure or −320.6° F. In general, refrigerants for removing heat at these temperatures are not conveniently available.

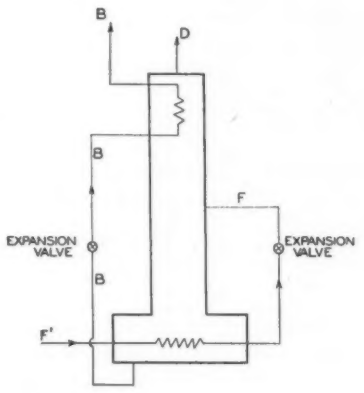


Fig. 8 — Refrigeration may be provided in the top of a stripping column as shown in Fig. 6 by using an expanded oxygen stream from the bottom of the column as shown here

One method for providing refrigeration at the top of a column producing nitrogen as an overhead product is to use an expanded oxygen stream from the bottom of the column as shown in Fig. 8. Here the column is operated at a pressure of 5 atm., under which nitrogen condenses at a temperature of −290° F. Liquid oxygen is withdrawn as a liquid from the still at 5 atm. pressure and is expanded to 1 atm. pressure, vaporizing slightly, the remaining liquid being evaporated at a temperature of −297.4° F., the boiling point of oxygen at 1 atm. pressure, around the tubes of an evaporative heat exchanger in the head of the column. The operation of this arrangement may be analyzed in the enthalpy-composition diagram in Fig. 9.

Consider the production of 99.0 per cent pure nitrogen from such a unit containing an infinite number of plates. In Fig. 9 the nitrogen product is represented by the point D, the air entering and leaving the still by the points F and F', respectively, the still liquid by point B and the oxygen product by the point B'.

With an infinite number of plates the point d, representing the overhead product, D, minus the heat added in the condenser, is located by extending the tie line through point F, as previously discussed. The still liquid, B, is equal to the difference between the air entering the still, F, and the overhead minus the heat added in the condenser, and therefore lies on the extension of a line dF'.

Also, the sum of the oxygen and nitrogen products, B' and D, must equal the entering air, F and therefore the point B' must lie on the extension of a line DF' and also on the saturated vapor line for 1 atm. pressure directly above the point B. A trial and error graphical solution, therefore, locates the points F', B, and B'.

The recovery of 99.0% pure nitrogen with infinite plates is only 73.8 mole % and the oxygen produced contains 51 mole % nitrogen. Thus while this arrangement may be used to produce pure nitrogen it suffers from the same defects as the stripping column in that only one pure product is obtained with low recovery.

As Ruheman[1] points out, this arrangement might be improved by stripping the nitrogen from the still liquid by superimposing a stripping column on the high pressure column. The heat liberated in condensing the nitrogen reflux in the high pressure column would be used to reboil the liquid in the still of the low pressure stripping column. This arrangement would produce a pure nitrogen and a pure oxygen product but at the same time a relatively large fraction of impure material as the overhead product of the stripping column. Thus the recovery of pure products would still be relatively small.

It is now possible, however, to use rectifying plates above the feed plate of the stripping column since reflux can be obtained by expanding a liquid nitrogen stream from the

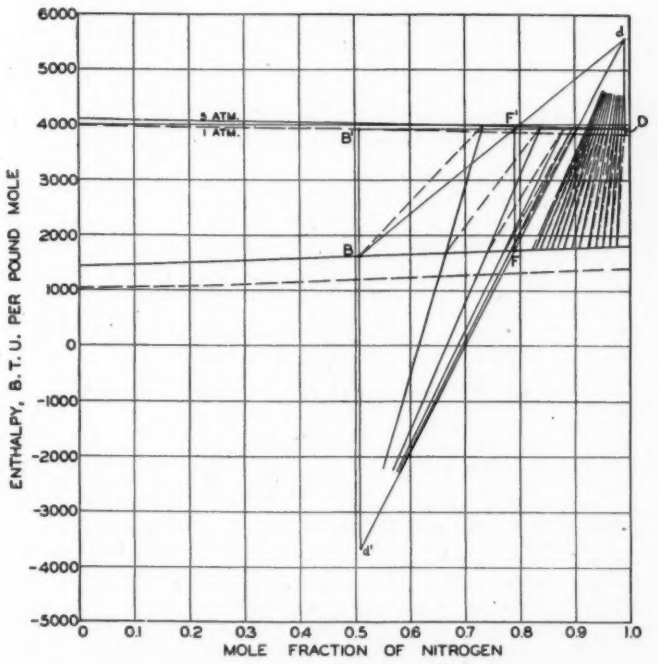


Fig. 9—Enthalpy-composition chart for calculations in connection with the stripping column in Fig. 8

high pressure column and introducing it as reflux to the low pressure column. This arrangement is known as a Linde double column and is shown in Fig. 10. The pure oxygen and nitrogen products are withdrawn as vapors from the still and overhead line of the low pressure column.

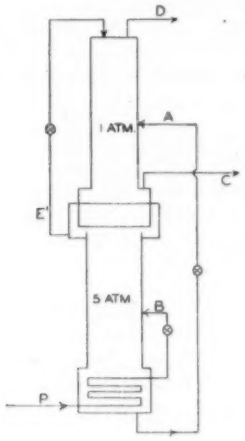


Fig. 10—Linde double column, in which a liquid nitrogen stream from the high pressure column is expanded and introduced as reflux to the low pressure column

The operation of a Linde double column is shown on the enthalpy-composition diagram of Fig. 11. The lettered points in the figure represent the lettered streams of Fig. 10. Consider the problem of determining the composition of stream *A* at minimum reflux when a Linde column is producing oxygen and nitrogen both of 99.0% purity and operating at pressures of 1 and 5 atm.

The entering air stream, *P*, lies on the line between points *C* and *D*, representing the outgoing oxygen and nitrogen products. The expanded air liquid entering the high pressure

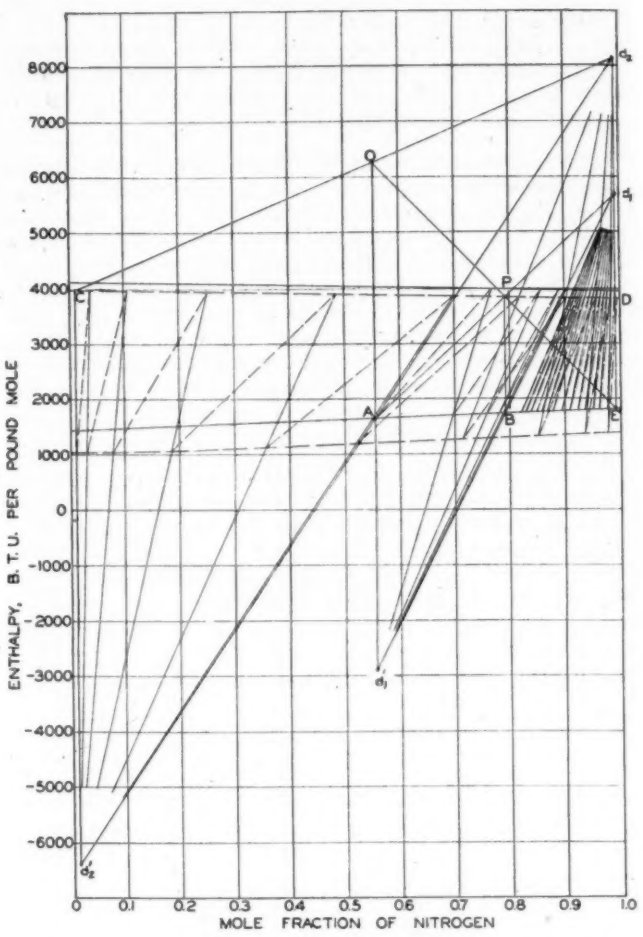


Fig. 11—The operation of the Linde double column shown in Fig. 10 is indicated by this enthalpy-composition diagram

column is represented by point *B*. By assuming a reflux ratio in the high pressure column the point d_1 is located. Since the still liquid, *A*, is equal to the difference between the entering air, *P*, and the stream *E'* minus the heat added in the condenser, the point *A* is located by extending the line d_1P to the saturated liquid line. The point d'_1 is then located directly below point *A* on the line d_1B.

The stream *P* is also equal to the sum of stream *E'* and the combination of stream *A* minus the heat added in the condenser. Thus the point *O* is located above *A* on the line *E'P*. The point *O* represents the still liquid *A* minus the heat added in the condenser when considering the high pressure column, but it also represents stream *A* minus heat added in the still when considering the low pressure column. Thus point *O* lies on the line between points *C* and d_2, representing bottom product, and the combination of streams *D* and *E'*, represented by point d_2. Point d_2 is thus located above *D* and *E'* on the line *CO*. When this point has been located, the bottom difference point d'_2 is located on the line Ad_2 directly below point *C*, as has been previously shown. When a tie line coincides with either $d_1Bd'_1$ or $d_2Ad'_2$, a condition of minimum reflux and infinite plates exists. This must be found by trial and error and gives a minimum oxygen content for stream *A* of 44.5 mole %. In this case the conditions of minimum reflux are approached in the high pressure column before it is obtained in the low pressure column.

Nomenclature Used in Equations and Charts in the Text

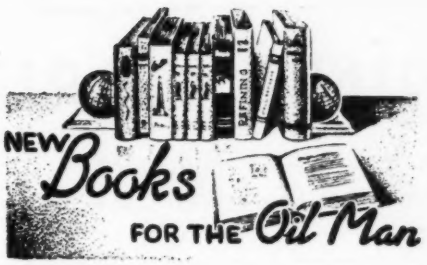
B=quantity of bottom products per unit time.
D=quantity of distillate product per unit time.
D_2=quantity of side-stream product per unit time.
d=difference point for rectifying section.
d'=difference point for stripping section.
d'', d_r=difference points for sections of fractionating columns other than rectifying or stripping sections.
F, F_1, *F* , F_2=quantity of feed streams per unit time.
H=enthalpy of vapor streams, Btu/lb.
h=enthalpy of liquid streams, Btu/lb.
L=quantity of liquid flowing per unit time in rectifying section.
O, *O'*=addition points for overall material and energy balances around a column.
Q=heat absorbed by a system from its surroundings per unit quantity of a stream.
R=quantity of reflux per unit time or moles of reflux per mole of distillate.
V=quantity of vapor flowing per unit time in rectifying section.
x=mole fraction of a component in the liquid.
y=mole fraction of a component in the vapor.

Subscripts

0, 1, 2, . . . =designation for specific plate in a column.
1, 2, 3=designation for streams 1, 2, 3.
B, *D*, *F*=designations for bottom product, distillate product, and feed, respectively.

Reference

(1) Ruheman, M., The Separation of Gases, Oxford Press (1940).



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"Helpful Trade Literature" items are usually available without charge, and can also be secured from the Reader's Service Department of Petroleum Processing.

Report Observations of Effects Of Fire and Atomic Bombings

Fire and the Air War, edited by Horatio Bond, 6 x 9 in., 276 pages, stiff cloth binding, illustrated, $4.00.

No one hopes more fervently than we that there'll never be another war. But if there is, we can be sure that our refineries and other industrial targets will not be spared from air attack, as they were in the past, with both explosive and incendiary bombs — and probably even atomic ones.

Fire and the Air War tells us what we might expect and what the results would be. It is an authoritative and factual account of the fires of war in England, Germany and Japan, of wartime fire fighting, and of the work of the fire protection engineers who helped plan the destruction of enemy centers and industrial plants. It is a compilation of the observations of eight fire experts, including Horatio Bond, chief engineer for the National Fire Protection Association. Also included in the complete text of the official reports of the U. S. Strategic Bombing Survey on the atomic bombing of Hiroshima and Nagasaki.

Although *Fire and the Air War* does not deal specifically with industrial targets, many of the experiences and observations reported will be of help and interest to refinery safety engineers studying the subject.

Analyzes Plastics Industry In Terms of Economic Values

Plastics Business, by Herbert R. Simonds and Joseph V. Sherman, 5⅜ x 8½ in., 439 pages, illustrated, indexed, stiff cloth binding, $5.00.

Although the petroleum refiner has been most closely allied with only one phases of plastics—synthetic rubber—the future trend will probably be toward even more mutual interests between these two industries. *Plastics Business* presents an exhaustive analysis of the plastics industry, its mechanics and development, and the economic aspects of its future role in the nation's enterprises.

Presenting the names of every significant manufacturer of raw materials, fabricators, equipment manufacturers and sales organizations, the book includes company statistics, sales and profits, prices, data concerning consumption of plastics, and it discusses the future. It treats of economics in terms of effects on other industries, the investor and the technician, foreign markets, and the growth of the plastics business.

The early portion of the book deals with with a fundamental description of the industry itself, its organization, and its materials. Two separate chapters in the latter half are devoted to plywood and synthetic rubber. Considerable data and statistics are provided in illustrative tables.

The authors are consultants in the plastics business. Mr. Simonds an engineer, is the author also of *Handbook of Plastics* and *The New Plastics*. Mr. Sherman, an industrial economist, was formerly vice-president of Economic Analysts, Inc.

New Almanac Is Statistical Record of Petroleum Industry

The Petroleum Almanac, 6 x 9 in., 420 pages, indexed, paper binding, $4.00; cloth binding, $5.00.

A statistical record of the petroleum industry in this country and abroad, *The Petroleum Almanac* consists chiefly of over 400 tables showing the economic significance of the industry, its place in the nation's distributive structure, tax revenues, and the growing importance of natural gas.

Many of the tables go back to the beginnings of the "coal oil" industry, some as far back as 1857. Natural gas well information dates back as far as 1899.

The book is divided into ten major sections on production, transportation, refining marketing, distribution, utilization, finances, labor, taxation, regulatory bodies, alternate sources of energy, prices and world petroleum supplies.

The information presented should make the book a valuable part of every oil executive's library.

It is a result of a year and a half of intensive research by the National Industrial Conference Board, an independent, non-profit institution for research and education in economics and business. Supported by nearly 3000 companies, trade associations, labor unions, government bureaus, and educational institutions, the Board has been in existence since 1916.

The book may be obtained direct from the publisher, The National Industrial Conference Board, 247 Park Avenue, New York 17, N. Y.

Helpful Trade Literature

Wyatt's, a 216-page book (9 x 12 in.) depicting pictorially the broad range of products that the company makes—including towers, vessels, and allied equipment. In addition, the book contains some 40 pages of valuable engineering reference tables. Distribution is limited. Address inquiries directly to the company on your business letterhead. Wyatt Metal & Boiler Works, PI Box 3052, Houston, Texas.

Our Third Report to Industry on Simplex Synthetic Rubber Insulations, tells why one company is "well pleased with synthetic rubbers" and is going to continue to use them in its products, even when natural rubber again becomes available. Compares critical properties and performance values of various synthetics (GR-S, Neoprene) with natural rubber. Simplex Wire & Cable Co., 79 Sidney St., Cambridge 39, Mass.

Allis-Chalmers Water Conditioning Chemicals and Equipment No. 28X6385, a 12-page instruction booklet for power plant operators, touches upon the importance of feedwater control the care of testing equipment, obtaining samples, test procedures and contains reference tables to help in reporting results. The Allis-Chalmers Mfg. Co., 710, Milwaukee 1, Wis.

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WIDENING HORIZONS

Views on Personnel, Management and Economic as Well as Technological Developments in Petroleum Refining and Natural Gas Processing: Comment from Readers is Invited

Refiners Should Be Informed On the Studies on "Jet" Fuel

STUDIES in the field of jet propulsion form no small part of the extensive research programs of the nation's oil companies. The oil industry has as much at stake in the problem as the military agencies which are also carrying on research. It will be called upon to furnish satisfactory jet fuels entirely different from the aviation gasolines now made for the conventional type of aircraft engines.

The federal government, through the laboratories of the National Advisory Committee for Aeronautics, is devoting almost full time to work on fuels for all three types of jet engines—turbine, ram, and rocket. NACA is working primarily toward the establishment of standards for the new jet fuels. The chief objective is concerned not with the improvement of octane ratings and the combatting of knock, but rather with how to make petroleum fuels burn faster, more efficiently, and with greater release of energy, especially at high altitudes.

Both the Army Air Forces and the Navy are also conducting considerable work in this field. Last summer the Air Forces made available to oil refiners 100 captured German jet engines as an aid in development work on fuels for jet propelled planes. The Navy's 1947 Congressional appropriation budgets a substantial portion of the funds toward research in this and other types of fuels for aircraft engines.

At present the exchange of data and information acquired in the government's studies in jet propulsion seems to be limited to the military authorities and to a few of the technologists with the larger oil companies who are directly engaging in this field of research. The basis for exchange of this data should be broadened to take in all the refiners. For all the groups concerned—the military, other governmental agencies and oil companies—study of jet propulsion is an entirely new field of research. Much that is being learned at this stage is fundamental in nature. It can have no particular military value, but it will be of value to oil companies generally in directing the line of their own study and thought on the subject.

The problem of the individual oil company will be how to supply in volume the best suited types of fuels for jet planes. The problem will be further complicated if jet fuels have to come from the so-called distillates, which will be in increasing demand in coming years for heating oils, Diesel fuels and other uses. Supplying jet fuels in the volume required in the event of a future war will be a problem for the entire oil industry, as was the case with aviation gasoline in the recent war. The industry should know, at all stages in the research program, what is being learned as to both the anticipated volume and the required characteristics of jet fuels.

What IS the Chemical Industry?

"Even defining the 'chemical industry' is becoming a problem. Petroleum refiners, rubber manufacturers, paper makers, tin can producers, manufacturers of electrical equipment—to name only a few—*all* are now participants in chemicals production. The interrelationship of products—both with respect to sources of raw materials and of use—is little short of bewildering".

The quotation is from a talk by Richard B. Schneider, of Arthur D. Little, Inc., entitled "Various New Aspects of the Chemical Industry", before the Noon Forum of the New York Society of Security Analysts, New York, Dec. 11, 1946.

High Wartime Plant Operating Rate Now Considered Normal

THE first full year after the war found the petroleum refineries of the country in most cases operating at almost as high rates of crude throughput as during the climactic months of the war. Demand for all oils in 1946 was within 1% of the wartime peak of 1945, accompanied, of course, by a considerable shift in relative demand for products. The Economics Advisory Committee of the Interstate Oil Compact Commission recently estimated that demand for all products in 1947 will be 3% greater than in '46.

When actual plant operations during the war averaged 95% or higher of the rated refinery capacity of the country, it was assumed this was an abnormal wartime operation. Many refineries processed more crude than their plants were rated to run. "Win the war!" was the slogan, no matter what the cost in plant wear. It was believed that, after the war, the refineries in general would drop back to considerably under rated capacity and there would then be ample opportunity for repairs and replacements.

However, in the peak motor fuel demand period of 1946 the plants were operating at 95-98% of rated crude capacity of the country. Refineries in general will have to operate at this rate or higher in 1947 to meet anticipated demand for all oils of 5,425,000 b/d. Total crude capacity of straight refineries of the U. S. is placed by the U. S. Bureau of Mines at not over 5,200,000 b/d.

So far as reported, refineries operated during the war at these high rates of crude capacity without undue damage to plants or equipment which called for abnormal replacements. Some engineers now believe that an operating rate of around 95% may be normal for a modern plant. Refineries of today are better designed and constructed and the materials and equipment used are of longer life than before the war. The use of alloy steels in place of carbon steels where high temperatures or corrosive conditions are to be encountered is a chief contributing factor in lengthening the continuous operating time of processing units.

During the war, plant operating bottlenecks were eliminated which had previously slowed down the rate of throughput. Modern plants are more complete as to various types of units and their operations more flexible and thus more quickly adjustable to current demand. Plant operating, maintenance, and repair crews are more skilled and better trained today.

This contribution of the engineering, operating and maintenance forces to hold plants to a high rate of operations is a tribute to the constant technological improvement in petroleum refining. To the individual company it is an important factor in keeping down operating costs, a material advantage in selling in today's highly competitive markets.

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Formula	$CH_3 \cdot CClF_2$
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Color	Colorless
Melting Point	—130.8° C
Boiling Point	—9.2° C
Density	1.194 at —10° C
Latent heat of vaporization	96 B.t.u./lb.

Vapor pressure (p.s.i. abs.):

—30° C	6.0
—10° C	14.7
10° C	31.2
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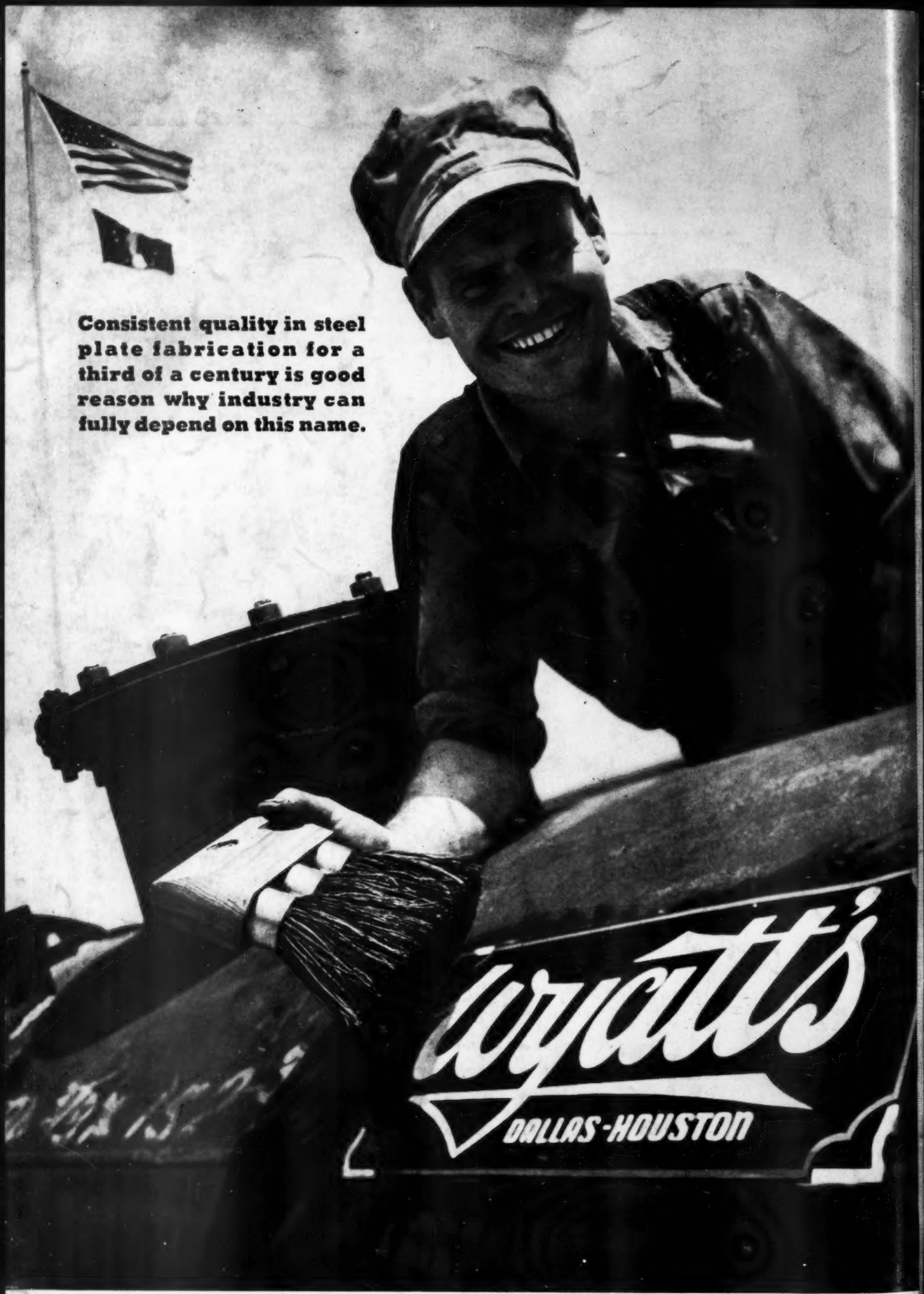
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